PRINCIPLES *and* PROCESSES OF LIGHT LEATHER MANUFACTURE

By

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INTRODUCTION

In spite of the rapid growth of scientific knowledge in the leather industry, many tanners are still somewhat averse to the exploitation of real scientific discoveries, or the encouragement of original research. There are few tanneries without a laboratory, and a fully fledged chemist; indeed, tanners would never dare to raise their heads at conventions unless they could boast of one, possibly two graduates from first class universities. To be without a chemist today is almost as bad as being without a bathroom in the home; it is considered a disgrace. Unfortunately, however, the highly esteemed chemist is usually fettered to his bench and spends all his valuable time carrying out routine analyses. Analysis has become a sweet sounding word to the tanner, a kind of fetish with which to ward off industrial evils. It is, perhaps, unorthodox, even a little radical to wonder if all these analyses are really necessary, and if so, whether it would not be possible to make use of simpler and quicker methods. The chemist is far too valuable a man to waste on hack work, and no matter how important that may be considered it can never be as vital to the industry as original research.

Of course the root of the trouble lies in the jealousy which exists, although but seldom apparent, between the practical, thoroughly experienced tanner and the academic chemist. He is mercilessly dubbed "theoretical" and that term has be-

come a sneer. How is it possible for him to be anything else but theoretical and to avoid developing that strange "scientific superiority complex"? He is seldom given the freedom or the time to study working conditions in the tannery, and it is rare, indeed that he visits other works. Thus instead of his experience and useful knowledge being increased and rendered valuable to the industry, it becomes strictly limited and stunted. We have scrapped the bound identured apprenticeship system which at least gave us fully experienced and often scientifically trained chemists, and substituted nothing in its place. True our universities and colleges are crowded with future chemists, but the sad truth is that these are nearly all destined to be hack workers. Stanley Baldwin once said, "modern industry depends upon coördination of many men's work, but you must maintain a large number of average men to make a brilliant man possible." That is a dismal truth which we have to face today.

To leave original research to national and international trade organizations is fundamentally unsound. The inventive genius in modern industry is a very rare bird indeed, and if by any chance he is discovered, then he is generally quietly suffocated. It is perhaps, a sign of the times that one very large English chemical concern has recently closed down its long term research laboratory to reduce expenses.

The life blood of the leather industry is imaginative research undertaken in the laboratory and the works, the two being regarded as one for the purpose of research. It sometimes happens that when the chemist does undertake any original work he is plagued by the tanner, his employer, for quick results. This means immature ideas, hasty conclusions and useless results; we are suffering from these today. Joseph Turney Wood could never have produced his brilliant work: Bating, Puering and Drenching, if he had not been encouraged by his uncle to develop ideas in the works as

well as in the laboratory, and to take years instead of months over his research.

It is high time that the technical chemist be allowed more opportunities for practical experiments, given more encouragement to develop new ideas and methods, and above all, promoted in time to a directorial position. The leather chemist should be better equipped than anyone else to act as one of the main balancing factors between labour and capital.

PAUL I. SMITH.

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PREPARATION OF SKINS FOR TANNING

SOAKING

THE real objects of this vitally important process are to clean the skin, wool or hair, also to soften and swell the fibres. Wrinkles and creases are often due to want of sufficient swelling and softening in the soaks, and it is no exaggeration to say that the success of depilation and liming depends to some extent upon the condition of the goods when they leave the soaks.

There is another point to consider, namely that loss of hide substance must be reduced to a minimum so as to avoid finished leathers being thin and empty, and showing some of the more obvious signs of bacterial damage. Tanners seldom realize that grain imperfections, particularly noticeable in the case of skivers, are often due to slight putrefaction changes in the soaks. Once salt has been dissolved out of the skin, and that occurs very rapidly, it becomes open to the action of putrefactive ferments which not only dissolve the soft mucous layer of the epidermis, but the actual cementing substance which knits together the fibres. Although foul soaks may result in softening of the skins, valuable and irretrievable protein matter is sacrificed, or broken down so that it will be rendered easily soluble in the limes.

The temperature of the soaks has a big influence on their softening and putrefactive action, and Procter considered

10 deg. Centigrade as the limit of safety: certainly above this figure there is danger of damage, especially when stale skins are being handled. It is a bad reflection on the intelligence of the tanner that a thermometer is hardly ever seen in the limeyard, and yet a few degrees increase in the temperature of the soaks may mean a big difference in the extent of putrefaction.

A HYDRO-EXTRACTOR FOR TREATING WET SKINS FOR THE SOAKS . . .

It is strange, but true that tanners do not like disinfectants, and they hold the view that they have an injurious action on goods in soak. This opinion seems hard to support, and there is in every tannery a prima facie case for their use. Suitable

A Typical British Drumshop . . .

disinfectants will not stain skins, swell them unduly or in any way interfere with subsequent processes, but they will control the multiplication of bacteria and their enzymes and reduce putrefactive action to zero. Any kind of disinfectant is not good enough, and it is waste of money to purchase a low phenol coëfficient product. Generally speaking it should conform to the following:

1. It should dilute with water and form a practically perfect emulsion or solution.
2. It should have a phenol coëfficient of not less than 5.
3. It should not solidify or separate at a temperature of 20 deg. Fahrenheit, or above.
4. It should be non-injurious and non-staining.

A coal-tar-creosote, cresol, phenol or similar emulsion or solution is preferable to one containing pine oil, rosin soap,

etc., as these latter substances are not suitable for use in the soaks. Certain salts and heavy metals are very effective inhibiters of enzyme activity and of the multiplication of bacteria, and some organic acids, particularly hydroxy and dibasic acids are toxic to bacteria and other micro-organisms. According to M. L. Isaacs, *Science* 75, 46 (1932), the bacterial cell carriers on all its functions through the activity of its enzymes, and the cell itself is inert (Duclaux Theory 1898), and it is therefore more important to use a disinfectant able to reduce enzymic activity to zero point than one which will destroy only a proportion of the bacteria present; disinfectants are often selective in action. Another important point to consider is that some disinfectants are rendered useless by the presence of a large proportion of protein matter in solution.

The author considers that an alkali-hypochlorite solution offers good possibilities for those soaks in which stale and hard skins are being treated. Except on a small experimental scale this method has never been tried out. Flemming recommends the use of sodium bisulphite, one pound per 100 gallons, and it certainly has a beneficial bleaching, cleansing and disinfectant action on light skins. One practical objection to the use of this chemical is that it deteriorates during storage, particularly under conditions present in many tanneries. Sodium fluoride, a powerful disinfectant and insecticide, is used occasionally in America, but never heard of in Europe.

The phenolic and cresylic body of disinfectants appear to offer the greatest possibilities in the tannery, especially as they are cheap, powerful, soluble and can be made non-injurious at workable concentrations. The tanner will be well advised to purchase this type of disinfectant in steel drums, say 25 or 50 gallon capacity. Purchase this way means a big reduction in costs. A concentration of one part per 1,000

should be safe and sufficient for the purpose of controlling the soaks, not necessarily making them sterile. There is an important difference here and one which must be considered. Sterility is not desirable. Apart from the use of disinfectants in the soaks, it is advisable to use a little when swilling down the limeyard during the hot weather. Bad smells may have been tolerated in the old days, but in these enlightened and scientific times they should not and need not be present. Insanitary conditions mean bad conditions.

Mere soaking in cold water is not enough to soften even fresh or wet salted skins, and they must be handled or worked in some way. Although large paddles are occasionally used for soaking light skins, the author still prefers the old fashioned pits. In these the goods have plenty of room for settling down, and the action of drawing the pit is very beneficial. Wet salted skins may require slightly longer treatment than fresh ones, and it is advisable to use several changes of water so as to remove completely all traces of salt. There is no doubt that the presence of salt in the skin before entering the limes is likely to interfere with their plumping action. At the commencement of soaking there is no harm done by employing a mellow, as distinct from an old soak,—that is, a liquor through which one or two packs have passed. During Summer weather even this modified practice is somewhat risky and it may be necessary to control its putrefactive action by the addition of a little disinfectant which must, of course, be added to the soak when the goods have been drawn.

The process which commends itself for all fresh and wet salted goods in normal condition is to use a fresh antiseptic solution each day until the goods are clean and soft. This method is simple, cheap and entails no risk whatever. For dry and obstinate goods the above method may not be suitable and here the addition of some kind of chemical assist-

ant is needed. In the author's opinion, an alkali is preferable to an acid, but considerable care has to be taken, and in the case of woolskins it may be inadvisable to use an alkali owing to risk of damage to the wool. Addition of .25 per cent on the volume of the pit is a safe proportion to use for either sodium sulphide or soda ash, the two best known assistants. As regards acids, lactic is by far the best and safest and five per cent on volume should prove quite satisfactorily. When chemical assistants are employed it is not necessary to use any disinfectants.

Some kind of mechanical handling is often necessary even when chemical agents have been added to the soaks, and some flint dried goatskins, light hides and kips are exceedingly obstinate. Dry drumming after two or three days in soak has been known to do valuable work, and sometimes it pays to break them over a beam with an old hand fleshing knife. Naturally all these methods add to production costs and it is doubtful if it really pays to handle these skins at all.

A very drastic mechanical treatment specially suitable for goatskins and reindeers, kips, etc., consists of a short run in a hide mill or faller stocks, but before the skins are worked they should first of all be well softened by soaking, with or without the addition of alkali, so that there will be no fear of cracking or in any way damaging the hard parts of the skins. Unless the goods are fairly soft, stocking is liable to cause a considerable amount of damage and should be resorted to only as a last hope. Apart from all other considerations, stocking is expensive both as regards labour and running costs.

Depilation

There are two general methods of removing the wool or hair, first, painting with alkaline sulphides and lime, second,

immersion in a strong sulphide solution. For sheepskins, painting is usually the method preferred as it enables the wool to be kept clean and in good condition. After soaking, which in many fellmongers' yards is carried out in a very perfunctory manner, it is usual to beat woolskins with a plunger pole and to brush the wool so as to remove all filth. These operations are then followed by soaking in clean water and hydro-extracting. As the wool holds a tremendous amount of water the skins should be allowed to drain for several hours before extracting. The best way to fold the skins is down the middle of the back, flesh in, and the number of skins depends upon the dimensions of the machine, size of skins and amount of water present. Fellmongers hold different ideas as to what constitutes a load, but in the case of woolskins there is no reason why the hydro should not be loaded up to within about four inches of perforations clear at the top of the cage, after the skins have taken up their position under speed. It is useless to give any definite instructions regarding running time and only the man in charge really knows the most suitable time. On no account must the skins be too dry before painting, otherwise it will be found that the depilatory will work unevenly.

Cages made of Monel metal, stainless steel and vulcanized rubber coated steel are all suitable for general work, and it is strange that these safe materials are not more widely used.

When the skins are taken out of the hydro-extractor all the creases should be taken out and the goods stacked up in low piles ready for painting. It is inadvisable to leave the folded skins lying about for several hours before shaking out the creases as this may mean the formation of permanent wrinkles and other grain defects. There is no risk of damage by using the hydro-extractor providing reasonable care is taken and all unskilled work placed under supervision.

The simplest way to make a depilatory paint is to mix

hydrated lime, slaked lime (carefully sieved) with enough sodium sulphide solution (26 deg. Twaddle) to make a smooth working paste. The skins should be laid out on a rough table and painted with a white wash brush so that an even coat of depilatory is given to the flesh. Care must be taken to prevent the wool being smudged with the depilatory and badly damaged. When painted, the skins need doubling up down the back and then stacking in piles, two to three feet high, and leaving for 12 to 24 hours. The piles should not be too high as otherwise heat will be generated and the skins damaged. The work of painting, folding and stacking requires a good deal of care and should be entrusted to intelligent men under the supervision of the foreman. It is advisable to arrange the work so that pulling or rubbing can take place the following morning. The wool must be kept clean and when a sufficient quantity has been collected it should be well washed, hydro-extracted for a few minutes and then dried off completely. Hydro-extracting is liable to remove some of the valuable woolgrease and the running time must be regulated to prevent undue loss.

Instead of sodium sulphide, reälgar or sulphide of arsenic may be used, and it is particularly suitable for gloving lambs, goatskins for glace, and certain grades of calf. It is claimed that the use of arsenic depilatories, also arsenic limes, results in a finer grain.

A good arsenic paint may be made as follows:

100 lbs. quicklime.
20 lbs. red arsenic.
50 gallons boiling water.

Tip the lime into a large size tub and pour over it just sufficient water for it to slake vigorously. When this has continued for half an hour add the arsenic and the remainder of the boiling water. Stir well for several hours and then allow to cool. Next day use the solution for painting; if too

thick add some water, or if too thin, then add a few pounds of slaked lime. It is advisable to run the thin paste through a coarse sieve so as to remove any unslaked lumps of lime likely to burn holes in the skins. When handling arsenic compounds it is very necessary to exercise great care to prevent accidents. The men should be provided with rubber gauntlet gloves, and the preparation of the arsenic-lime depilatory carried out in the open air.

Depilatory action is always quicker and cheaper if it can be carried out by immersion in a strong sulphide solution, but this method is not practicable if the hair or wool is of any value. A depilatory lime may contain from one to two per cent sodium sulphide crystals and three to five per cent lime on the hydro-extracted weight of stock. The best plan is to slake the lime in a pit by just covering it with sufficient water to enable it to work vigorously over a period of twelve hours. At the end of that time the desired volume of water should be added and the liquor well plunged up or agitated by some mechanical means. Agitation by means of compressed air is a most efficient and economical means of agitation. To ensure the best results it is advisable to stir up the lime liquor either by hand plunging or other means, add the sulphide solution (26 deg. Twaddle) and then agitate the liquor again for the same length of time. This may seem like double and unnecessary work, but in practice it proves well worth while. The skins should be thrown into the liquor one by one and pushed under the surface with a long pole. Some tanners allow the goods to remain for six hours for drawing, others only two hours, but all manner of variations are capable of good results. In the case of calf, kips and light hides, it is recommended to add a further amount of sulphide after the first draw, about one quarter of one per cent should prove sufficient. At the end of 24 hours the hair or wool will generally rub off very easily either by hand or machine.

Quite recently the use of enzymatic unhairing agents has been extended. Most of the preparations now on the market are based on the discovery by Dr. Röhm, who in 1913 invented and patented the use of proteolytic enzymes to be worked in conjunction with alkalies for unhairing. It is claimed that the greatly improved modern enzyme unhairing agents not only unhair, but swell and bate the skins. The advantage of this new method is that it is particularly suitable for fine grain leather, goatskins for gloving purposes and glacé, calf for fine hat leathers, box and willow, and the process may be carried out in pits or drums. Frequently the process is carried out in two stages, the first being concerned with swelling, the second, unhairing and bating. There is plenty of room for improvement in these new unhairing compounds, and some are very unreliable, especially when carelessly used by men to whom ounces mean very little.

Liming

After depilation comes liming.

A good quality lime (90 per cent calcium oxide minimum) will do its work well without any assistance in the case of ordinary goods, but for stale skins, thin, impoverished and badly cured goods it is advisable to sharpen up the limes with a little sodium sulphide or soda ash. A vexed question for the tanner is to decide what excess of lime is necessary for thorough processing. Only a small percentage of lime is soluble in water (1.25 grm. per litre) but it is essential to have present sufficient to replace the lime absorbed by the skins. Four per cent on the extracted weight of the skins allows a large margin for replenishment, and two and one-half per cent should prove sufficient providing the liquors are not exhausted by being too long in use. In any case this is an evil practice and results in tender and inferior leather.

The action of lime is to swell the fibres, remove the epidermis and certain substances between the fibres. It also converts a proportion of the natural grease into insoluble calcium soaps which are removed during scudding. A saturated and perfectly sterile solution of lime will not do such good work at the commencement of the process as a mellow lime in which enzymic ferments and ammonia appear to play important parts. In these worked solutions a proportion of the lime is in colloidal suspension and readily absorbed by the skin.

There are countless systems of liming, and every tanner thinks his own method is best, but fundamentally there is little real difference between them. They depend upon the action of liquors of varying age, working always from the oldest to the freshest. Excellent results can be obtained from a three pit liming system, the first being a mellow lime; second, a medium, and third, a fresh, sharp lime. After once working round, the first is run off and becomes the new lime; then the second, the mellow and the third, the medium lime. If more pits are used a longer range of mellow limes is possible. There is no hard and fast rule for liming as everything depends upon the kind of goods to be worked and the type of leather to be made. Sheepskins for splitting require a good sharp liming to produce a firm pelt for the band knife machine, and this means that time in mellow limes must be curtailed to a minimum. On the other hand, gloving leather and clothing leather are best worked in fairly mellow limes containing a little sulphide. Calf for box and willow generally do well in a short system of medium and sharp limes, and goatskins for glace kid in the longer and milder working ones. The limeyard foreman has a most responsible position, but too often he is ill equipped for his job which he works by rule of thumb.

A great deal of the success of liming depends upon the

agitation of the liquors and the handling of the goods. One draw a day should be regarded as a minimum and the goods allowed to drain for at least three hours. Hand plunging, unless very energetically carried out, often fails to stir up all of the lime at the bottom of the pit, and agitation of the liquor by means of a small propeller at the bottom of the pit works wonders and ensures uniform suspension of lime throughout the volume. Instead of prolonging the period of liming, better results can often be obtained by employing more scientific methods of agitating either the goods or the liquor, preferably both.

Paddle liming will give satisfaction in those cases where precautions are taken to prevent grain damage through the action of the wheel. One tanner has experimented with paddle wheels covered with soft vulcanized rubber and this is an idea worth considering.

Goods allowed to drain should be protected with sacks soaked in lime. The action of air on the lime saturated grain of the skin causes what is known as "lime blast," a common defect which is often never noticed until the skins are tanned. In the case of chrome tanned goods, lime blast is only seen in the finished warehouse and by that time it is too late. The use of pigment finishes can, of course, cover up this kind of grain defect, but not completely. The heaps of skins should be first covered over with skins, flesh side outside, and then the sacks. Colt is fairly common amongst sheepskins and it is a peculiar condition due to structural changes in the skin brought about by bacterial changes and the partial saponification of natural fats present. According to Seymour-Jones, colt is due to an adipose degeneration of the fat-cells, which results in hydrolysis of the fat and crystallization of the fatty acids set free.

Liming of colty skins is very difficult, and the use of sodium sulphide is recommended to the extent of one-quarter

of one per cent on the fellmonger's weight. Time of liming should be curtailed to prevent undue swelling and old limes must not be employed. The best practice seems to be to commence with a medium sulphide lime (two packs having passed through) for three days with one or two draws a day, and then to finish off in a new sulphide lime for two days.

The author considers that a considerable amount of time and material could be saved if the tanner used a uniform hydrated lime instead of quicklime. This basic chemical often contains limestone, gravel, and many other impurities of a definitely injurious nature. The presence in the lime of incompletely calcined pieces likely to slake very slowly has been known to cause burns in the skins. Hydrated lime is, of course, more expensive than quicklime, but as it is fairly pure, great economy may be exercised, and by its use it is possible to exercise more control over liming.

Corrosion of Metal Plant in the Limeyard

Unfortunately very little attention has been given to this important subject, and yet corrosion of ferrous metals, concrete, cement and wood surfaces causes a considerable amount of damage to goods by staining, and also results in costly depreciation of fittings, etc. It is high time that this matter was fully investigated and tests made to determine the degree of corrosion suffered by the materials used in building construction and fittings, utensils and even clothes.

In reviewing this question of corrosion in the limeyard the chemist has to consider it under two broad headings:

1. Atmospheric corrosion.
2. Corrosion due to actual immersion in solution.

The air of the limeyard contains ammonia, hydrogen sulphide, sulphur dioxide and other gases responsible for corrosion, and of course a considerable amount of water vapour.

In order to find out the most serviceable metals, or substances generally immune to atmospheric action, tests must be carried out in the laboratory and also the works. First of all, exposure tests in the limeyard should be conducted over a lengthy period, not less than six months. The object of these should be to discover the best metals and other basic substances, and the finest protective coatings for these surfaces. Tests in the laboratory might well be confined to stagnant and agitated solutions of the same character, temperature, as the lime liquors in general use. These tests should later be extended to the limeyard and standardized pieces of metal and other materials exposed to the action of the various kinds of lime liquors and other solutions used. From the mass of evidence collected over several months, this work cannot be hurried, it should be possible for the chemist to advise the tanner regarding the most suitable metals, woods, cements and other substances for use in the limeyard, and also the best means of protecting these against atmospheric gases and contact with solutions.

According to A. S. White (Ramsay Laboratory of Chemical Engineering, University College, London), the following factors must determine choice of metals for plant construction and fittings.

1. Suitability: its corrosion resistance both general and particular, the possibility of a contaminated product, and the physical properties of the material (its strength, ease of working, etc.).
2. Availability: the ease with which the material can be obtained commercially in the desired forms, ease of replacements, etc.
3. Economic factors: its initial cost, rate of depreciation, scrap value, etc.

Aluminum and its alloys, Monel metal, stainless steel and anti-corrosion rubber lined metal, chemical resisting cements,

stoneware and wood treated with metal or plastic materials are all new and worthy of consideration by the tanner. Apart, however, from the use of the new materials, valuable work may be done by testing the comparative value of protective paints, lacquers, etc. The best known of the anti-corrosion paints are, of course, the oil paints, with lead, zinc, or iron pigments for finishing coats and red lead for priming. According to F. Ohl, *Chemisch-Metallurgische Zeitschrift, Die Metallborse,* Feb. 21, 1934, p. 226, their anti-corrosion action is due mainly to a reaction between the pigments and the oil binder, insoluble-lead oil aggregates being formed from the glycerides of the vehicles; these are more or less viscous, flexible and resistant to atmospheric and chemical influences. Bituminous paints are now being widely used to afford protection against chemical corrosion, and they can be used either alone or in conjunction with lead-oil priming. Bitumen paints are subject to disintegration under the actinic action of sunlight, but by mixing aluminum powder with bitumen this disadvantage is overcome and a paint giving a lasting and bright metallic surface results. Silicon paints are alkali resisting and should prove very suitable for painting purposes in the limeyard.

Value of an Efficient Pumping Service

Every limeyard should be provided with a good pump as by its use liquor can be easily and quickly transferred from one pit to another with ease and rapidity. Most tanners use the ordinary reciprocating type, but the author considers that the centrifugal pump is in many ways preferable for the purpose. It is cheaper, occupies a smaller space and has a steady discharge and freedom from pulsation. It is well fitted for direct drive by motor, turbine, gas or oil engine, and as it has no internal valves likely to be clogged by the

entry of solid or gritty matter in the flow, maintenance work becomes fairly simple. The tanner interested in a new pump will do well to consider the advantages of the latest self-priming centrifugal pump made of material likely to with-

Paddle Liming in an English Tannery

stand alkali corrosion. The life and service of the pump depends a good deal upon its position in the limeyard, that is, whether it is well lighted, dry and reasonably protected by some kind of paint to withstand atmospheric corrosion. Regular attention and inspection are vitally necessary to ensure that the pump is always in good working order.

Chemical Control of Liming

Strict laboratory control of limeyard processes is very necessary to ensure uniform results. Apart, however, from routine analysis to determine the purity of raw materials and

alkalinity of liquors, tests might well be made directly after lime liquors have been well plunged up, or otherwise agitated to find out the dispersion of insoluble lime in solution and rate of settlement. Too little attention is attached to these points, but they are of considerable importance as unless liquors are well agitated before throwing back the goods, the action of the lime will be incomplete. Simple but useful tests might be carried out by the foreman by filling a graduated cylinder with freshly agitated liquor and then measuring the sediment at the end of five, ten, fifteen and twenty minutes. These tests are rendered particularly valuable if samples of liquor are taken at different depths in the pit, say on the surface, at a foot below, and three feet below.

Rounding or Trimming

This preliminary operation is carried out by hand and it is very important to the tanner that the workers (usually classed as unskilled or semi-skilled) should be really skilled and show more than the ordinary amount of common-sense in their work. The offal must, of course, be cut away, but at the same time the shape of the skin has to be made neat and presentable and as much footage left as possible. If the worker uses his knife too freely because he is either careless, or lazy, then this means a heavy loss to the manufacturer. Waste of two or three square inches on every skin soon mounts up when multiplied by thousands.

It shows great want of foresight on the tanner's part that trimming, or rounding is considered of such small importance that the work is frequently given to men too incompetent to do other jobs in the factory. This work is skilled and should be paid at good rates, then and only then, will the tanner get the best results, results which will well repay him.

Preservation of Glue Stock

Limed offal is a valuable by-product and it should be carefully preserved until disposed of to the glue manufacturer. In the summer the pieces need wetting down with freshly made lime water, and the stock will deteriorate unless it is frequently turned over with a fork. Offal from calf, goat and sheepskins should all be kept separate and stored in shallow concrete or cement troughs well out of the direct rays of the sun. The following extract from the author's book on "Glue and Gelatine" is worth quoting:—"When a large heap of skin pieces is left exposed to the weather for any considerable time, those pieces on the top become bone-dry and assume an objectionable bluish colour, which gives the buyer a bad impression; there is also a considerable loss in weight due to the continual draining of the stock. As the material is usually sold by the ton, this diminution represents a serious pecuniary loss to the tanner. In view of these facts, it is a good plan to have the stock turned over with a fork once a day, so that the weight may be kept more or less constant and risk of discoloration considerably diminished. The tanner is sometimes confronted with the fact that the glue manufacturer, through bad trade, or other causes, cannot deal with the whole of the former's stock, with the result that he is left with a considerable stock of putrescible material, likely to diminish in value if kept for any long period. In this case, it is advisable to make up a fresh lime liquor in a pit, 25 pounds of quicklime, and the pit half filled with water.

"The author has found that hide and skin pieces will keep in excellent condition in the above saturated solution for six months, at the end of that time the pieces have a tendency to become 'meally' that is, they seem to lose their characteris-

tic 'fleshy' nature owing, no doubt, to intensive hydrolysis, and can be easily broken up into a kind of granular powder or meal by rubbing." A solution of boric acid, 5 lbs. per 1,000 gallons of water will also preserve glue stock.

Fleshing

This is usually done by machine which in principle is fairly simple. The skin is pressed flesh side up against a cylinder with spiral blades arranged right-handed on one half and left handed on the other so as to extend the hide sideways as well as scrape it. An inflated, or soft rubber roller is used to keep the skin in close contact with the knife or fleshing roller. A great deal of the success of fleshing by machine depends upon the condition of the skins beforehand. They should be firm enough to stand up to the knife blade and to flesh cleanly, and this is only possible if they have been allowed to remain in small heaps for twenty-four hours or so and well covered up with bags. It is always better to leave a little flesh on the skin rather than leave it too clean, and the man in charge must be encouraged to use his judgment regarding pressure for different kinds of skins.

Fleshings from the machine contain a considerable amount of valuable fat and they can be boiled in vats and the grease recovered.

Deliming

This is necessary to remove the bulk of the alkali from the skin, but enough should remain so that the skin registers an alkaline (faint) reaction when it goes into the puer or bate. A large number of acids and acid salts are used to remove the lime and good results may be obtained with several of them. J. T. Wood favoured a weak solution of hydrochloric acid, 28.5 Twaddle, 4000 c.c. per 250 kilo of wet pelt,

just sufficient to delime the surface of the skin and prepare it for the puer. Strong mineral acids, although cheap and quick, are liable to make the grain rather coarse and they must be used with great care. In the writer's opinion the organic acids, lactic, acetic and formic are safer than the mineral acids and give better results, particularly for good quality skins. Using formic acid, one pint of the commercial acid for each ten dozen average pelts is recommended for sheepskins to be puered with either natural dung or artificial bate. The goods should be well washed in a paddle with running water for ten minutes, then half a pint of acid (diluted with water) added and the goods run for half an hour. At the end of that time the remainder of the acid should be added and at the end of three quarters of an hour, total time, the skins tested (cut surface) with phenol phthalein.

It usually happens that a little free lime shows but this does not matter as the puer continues the deliming action, and in any case goods work better in the puer if their reaction is on the alkaline rather than the acid side. The author has found that a mixture of formic and acetic, equal parts, gives slightly better results than the pure acid. Acetic anyhydride also gives good results but this chemical is rather expensive. Procter recommends lactic acid, about 2 lbs. per 100 gallons, but although this acid is excellent for the purpose it is not very greatly used in the light leather industry in England.

M. C. Lamb classifies the acids in degrees of safety.

1. Boracic or Boric.
2. Lactic.
3. Formic.
4. Hydrochloric.
5. Butyric.
6. Sulphuric.

He stresses the fact that the amount of acid used should

be calculated to soften the water as well as delime the skins, and considers that one and a half hours is the safest time.

Deliming is best carried out at 80 to 90 deg. Fahrenheit and the paddle should be provided with a steam coil at the bottom covered over with protective wooden laths. In some tanneries the paddles are provided with automatic temperature controls and this practice, although somewhat costly, eliminates all risk of damage through over-heating and ensures uniform results.

Choice of acid depends a great deal upon the nature of the goods processed and the kind of leather to be made, generally the use of a mild swelling acid, such as hydrochloric or some organic acid is preferred. After deliming, it is necessary to wash the skins, preferably in soft water for twenty minutes before puering. Ammonium butyrate, ammonium borate and ammonium chloride as well as borax have all been used, but except in the case of borax, they appear to offer few advantages over the cheaper acids. Borax is very useful for fine calf but it is, unfortunately, rather expensive. Boric acid may, however, be used for the same purpose in conjunction with formic acid, the proportions being two parts of boric and one part of formic.

PUERING

The neutralization of free lime in the skin continues during the process of puering or bating, and it is not usually complete until after drenching. Apart, however, from the chemical action of the soluble salts present in the bate, a vitally important change in the actual structure of the skin takes place. According to J. T. Wood, "The object of bating or puering is to render the skins, and the resulting leather, soft and supple. Skins which have undergone the liming process, must be thoroughly freed from lime before

going into the tan liquors, and for light and soft leathers, they must be reduced or 'brought down' so that the elasticity or resilience of the skin fibres is gotten rid of, and the skin, when tanned, can be stretched without springing back."

There is no doubt that even in the present advanced state of knowledge relating to this process, a considerable amount of doubt exists concerning the complete action of a bate. It is not just a question of chemical deliming, removal of the remains of the hair follicles, fat glands, or even the digestion and removal of the elastin fibres which Procter says are very abundant in the grain layer and prevent it from spreading. The author considers that sufficient attention has not yet been paid to the mechanical action of solid particles in the liquor. A perfectly clear bate will not reduce the skin in quite the same way, or as easily as one containing matter in suspension. The efficacy of any bating preparation appears to depend upon the completeness of these four inter-related actions.

1. Chemical action of the soluble salts present.
2. Action of the organized ferments.
3. Action of unorganized ferments.
4. Physical action of matter in suspension.

Fresh bate is faintly acid to litmus but the pH is reduced as the free organic acids become neutralized by the lime in the skins. This drop from faint acidity to neutrality is very important and depends largely upon the condition of the skins after deliming. It is undesirable for the skins to enter the puer in an acid condition as this slows down the activity of tryptic enzymes and results in irregular action of the liquor. Some tanners seem to forget that absolute uniformity in the condition of the puered goods is only possible if liming and deliming are so regulated that the percentage of free lime in the skin varies very little from pack to pack. The great difficulty experienced when dealing with colty sheep-

skins is largely due to the fact that these contain abnormally high proportions of free lime. Skins given a short liming always fall easier and quicker than those given a prolonged treatment.

Proper bating is only possible if the right kind of bate is used, the optimum temperature for enzymic activity maintained and the goods kept continually on the move. Failure to keep the skins moving results in the collection of countless billions of bacteria in the folds of the skin and causes what is known as flaking, really a bacterial damage to the fine grain.

Dog dung is still being used for puering goatskins for glace kid and sheep grains for skivers, but although natural excrement has a more complete falling action and produces a slightly softer leather, the arguments in favour of a standardized artificial bate are almost universally recognized. The usual practice when employing excrement from the kennels is to store it in a wooden vat sunk in the ground so that it is kept cool, and provided with a heavy wooden lid. Perfectly fresh dung does not seem to act so well as when it has been kept for a few days. It is, however, very important that the dung should not become discoloured and putrid otherwise it will cause the skins to putrefy and spoil. During the period of storage, a good deal of the solid particles present in the dung settles down to the bottom of the vat which requires cleaning out every month or so. Straining of the dung is often recommended, but in the author's opinion this is seldom done in practice, and the settling in the vat prevents sharp pieces of bone and stone from entering the puer paddles. In any case, solid particles of matter in the puer have a most beneficial action on the skin and should not, therefore, be excluded. Wood recommends 165 lbs. of dog dung for 25 dozen average sheep grains, weighing 1100 lb. (wet state) in a paddle with a capacity of 200 gallons. The author's experience is that these proportions will give good

results under certain conditions, but everything depends, of course, upon the nature of the dung, its condition and the general condition and nature of the goods to be puered. The foreman in charge of puering is the only man in the real position to give an opinion concerning the most suitable proportions of natural bate to use for various classes of goods. He knows more from instinct than pre-knowledge of conditions that even the weather has an influence on the process of puering and during the summer months goods come down very easily. When using natural dung the greatest care has to be taken to avoid damage to the goods, and in view of the considerable risks involved it is rather remarkable that it still finds some use in the modern tannery.

Many of the artificial bates now in wide use in this and most other countries consist of enzyme preparations, and although a number of them are secret compounds, they are based mainly on the discoveries of J. T. Wood and Dr. Röhm who first used the pancreatic enzyme on a practical scale. Frequently bates consisting of deliming salts with pancreatic enzyme can be used more effectively with bates consisting of bacterial preparations, but the practical man has to discover for himself the most suitable formula. It is very important, however, that the local conditions should be carefully studied before making a choice of bates. The hardness of the water, the liming and general quality of the skins need to be taken into account. The best condition of the skins for puering with artificial bate is when the grain surface is just clear of lime and the cut surface slightly alkaline as shown by Phenolphthalein.

After deliming, some tanners paddle their goods in warm water so that when they enter the bate they do not lower the temperature. A slightly better method is to make allowance for the drop in temperature by warming up the puer four or five degrees above normal. The correct quantity of

bate, this varies considerably according to the kind of goods and their condition, is made into a thin paste with warm water, 98 deg. F. and added to the paddle containing used bate liquor, some of which should be run off after working a pack. The optimum temperature for working appears to be about 95 deg. F. for pancreatic enzyme bates, and perhaps a little lower, 80 to 90 deg. F. for bacterial bates. Movement of the goods is necessary to effect even action of the bate and a paddle appears to be capable of more uniform and better results than is possible with a drum, although the latter is widely used for heavy skins which do not require such complete puering as light skins.

After puering the goods are generally scudded, either by hand or machine, to remove the pigment granules, wool or hair roots, dissolved skin rendered soluble by digestive action of the enzymes, and general filth. According to J. T. Wood, an analysis of scud from English sheep grains showed about 1 per cent skin substance, and 7.9 grams of fat per litre. Scudding is an important preliminary process and unless it is carried out very thoroughly the clean colour of the grain surface is liable to be affected. Complete scudding by removing free and saponified fats enables tanning to proceed normally. In the author's opinion, the goods should be paddled in warm water 95 deg. F. for five or ten minutes before scudding as this helps considerably to remove some of the filth. The addition of a trace of disinfectant in the water say four ounces of trichlorphenol to a paddle full of warm water will prevent prolonged digestion to some extent. After scudding, the goods should again be washed and then drenched.

Drenching

A fermented bran drench containing small quantities of weak organic acids, roughly 1 to 3 per cent, of which about

1 per cent is lactic, and evolving gases, has a very beneficial action on the skin. Apart from the mechanical cleansing action of the bran particles, the weak acids finally remove all traces of lime and the gases distend the fibres. The bran drench may be suitably adapted to meet all requirements, and and in some cases it is sufficient to paddle or drum the goods in a sweet (unfermented) infusion of bran, but for very soft, supple leathers, a sour drench is usually necessary. A temperature of 95 deg. F. is the most suitable for fermentation and the bran soon begins to ferment and continues to act fairly vigorously for as long as 24 hours, or even longer. The amount of bran employed varies considerably, but 1 per cent on the pelt weight of goods may be taken as an average. Some motion is necessary during the early stages of fermentation, but it is undesirable to keep the goods continually on the move during the whole period of drenching. Like puering with natural dung, drenching is by no means a safe process, and constant supervision is necessary to avoid the drench "turning" during thundery weather. This so-called "turning" is often an intense butyric fermentation and results in swelling, and if prolonged, actual digestion of the skins. Apart, however, from butyric fermentation, the drench sometimes goes bad as the result of the activity of certain chromogenic bacteria and in this case the solution becomes alkaline, putrid and evil smelling. If either trouble is suspected, the goods should be at once removed and pickled. This is the only possible means of preventing very serious damage, especially to sheep grains. In the author's opinion a great deal of trouble can be avoided by seeing that the drench paddles are well scalded out before use so that they are practically sterile when the bran is mashed. The danger of pollution by ferments and bacteria is always present, and safety can only be assured if the paddles are thoroughly scrubbed out with clean brushes, then well scalded. There

seems no reason why a good chlorine disinfectant should not be used, provided the paddle was well hosed with plenty of water, not necessarily hot.

The author has found that useful drenching action may be carried out by drumming the goods in a solution containing 1 per cent lactic and ½ per cent acetic acids and 4 per cent sawdust. The addition of sawdust is useful owing to its mechanical cleansing action, but it must be clean and free from dirt or metallic particles, usually iron.

The extent of drenching depends largely upon the condition of the skins, and the kind of leather to be used, but prolonged drenching in a sour drench is risky and liable to produce spongy leather. During the winter months, it is possible to give the goods a longer drench with safety, but the decision should be left in the hands of the foreman in charge.

Steam Economy in the Wet Shops

Live steam is commonly used in the puer and drench shops as a means of heating up solutions, but it is a wasteful and primitive method. A steam coil in the false bottom of the paddle is a far more economical and sensible method, especially if an efficient temperature control is provided to make the whole process easy to regulate, almost foolproof in general practice. Whilst discussing this question of steam heating, brief mention should be made of steam distribution in the wet departments. In a large plant there are often miles of steam pipes running in all directions, and in many cases they are often inadequately protected or insulated, if at all, so that both temperature and steam pressure fluctuate a good deal from the time it reaches the furthest point from the boilers. At a time when strict economy is necessary to reduce working expenses, constant

supervision of the plant is essential if the steam heating plant is to prove really reliable and economical to run. Insulation or lagging of the pipes should be carried out with a mixture of asbestos, magnesia and clay, etc., and they should be well packed and adequately protected by means of a close wire mesh covering. It is no uncommon sight to see the insulated wrapping crumbling to pieces and showing the iron pipes red with rust. In the case of derelict buildings, empty rooms, etc., the steam might well be shut off from that section altogether, but here, of course, care must be taken to see that the fittings are not allowed to deteriorate.

Pickling

This is a highly important preparatory process for tanning, especially chrome tanning, in which case the free acid in the skin plays a valuable part in controlling the action and absorption of chromium salts at the commencement of the process. Apart, however, from practical considerations relating to tanning, either vegetable or mineral, pickling is important as a means of preserving the skin. During the ordinary pickling process using sulphuric acid and salt, the skin absorbs hydrochloric acid formed by the reaction and the amount absorbed is largely dependent upon the concentration of salt in solution. In many cases, hydrochloric acid can be substituted for sulphuric acid and this is advisable when the goods are to be chrome tanned with basic chromium chlorides. The author has found that sulphuric acid gives slightly better results in the case of sheep grains and roans intended for vegetable tanning than hydrochloric acid. According to Winnifred B. Pleass, Ph.D. J. S. L. T. C. April, 1936, 1 per cent sulphuric acid and 10 per cent salt should be satisfactory when the ratio of liquor to goods is 6:1. When the ratio of liquor to goods falls, a

higher concentration of acid and salt may be necessary; when the ratio is 3:1 about 1.2 to 1.5 per cent acid and 12 per cent salt would be a convenient concentration. Optimum concentrations for a pickle liquor after use are 0.8 per cent sulphuric acid and 9 to 10 per cent sodium chloride. (Percentages refer to parts by weight per 100 parts by volume of solution.) Procter considers that 80 lbs. of salt and 7.5 lbs. sulphuric acid per 100 gallons of water suitable for general work. A common formula for pickling sheepskins is 10 deg. Twaddle for the liquor before use containing about 1 per cent sulphuric acid. Formic acid is also used and it gives excellent results as confirmed by Seymour-Jones and other workers, and it seems particularly suitable for goods intended for high class fancy leathers. One advantage which formic acid possesses over sulphuric acid is that it has no damaging effect on the grain if any trace of lime remains after puering and drenching. The presence of lime means that in the case of a sulphuric acid pickle, a form of lime-blast or precipitate of calcium sulphate is thrown down. Pickling with formic acid is best carried out in a drum as the minimum quantity of acid can then be used and the time considerably reduced. Proportions of 1 per cent formic acid, (40 per cent strength) 5 per cent salt per 100 lbs. weight of limed pelt are recommended, but in general practice it is advisable to increase the proportion of formic to 2 per cent on the limed weight for the best results. This formula gives excellent results if followed by paddle or drum tanning with sulphited quebracho and myrobalans, chestnut extract or sumac, and for hatter calf it is highly recommended. Unless the goods are to be stored for any length of time it is unnecessary to pass them through a strong brine (20 deg. Twaddle), but if they are to be stored then this is essential, and they should be allowed to remain in the brine for at least twenty minutes.

It is a well known fact that the ordinary sulphuric acid pickle followed by the strong brine is not able to retard fungoid growth. A formic acid pickle will, however, give full satisfaction in this direction as formic acid is an excellent antiseptic. Recently work has been done with the idea of evolving a safe formula for a storage pickle, and according to Winnifred B. Pleass, the addition 0.01 per cent beta-naphthol, trichlorphenol, paranitrophenol will prevent the appearance of fungi. Seymour Jones some years ago advocated a sterilizing pickle of 1 per cent commercial formic and 0.0002 mercuric chloride, but there is no doubt that this disinfectant is too dangerous for general use, and the author considers it rather doubtful that this small concentration of the mercury salt would prevent the appearance of moulds and mildew, especially during the summer months. Conditions of storage do, of course, influence the growth of fungi, and it is very important that the skins should be stored in a cool, dry place. Increase of temperature causes serious trouble which usually becomes evident in discoloration, partial swelling and crystallization of the salt. The latter is fairly common and it may be serious as the crystals have a tendency to make the skins spongy and porous.

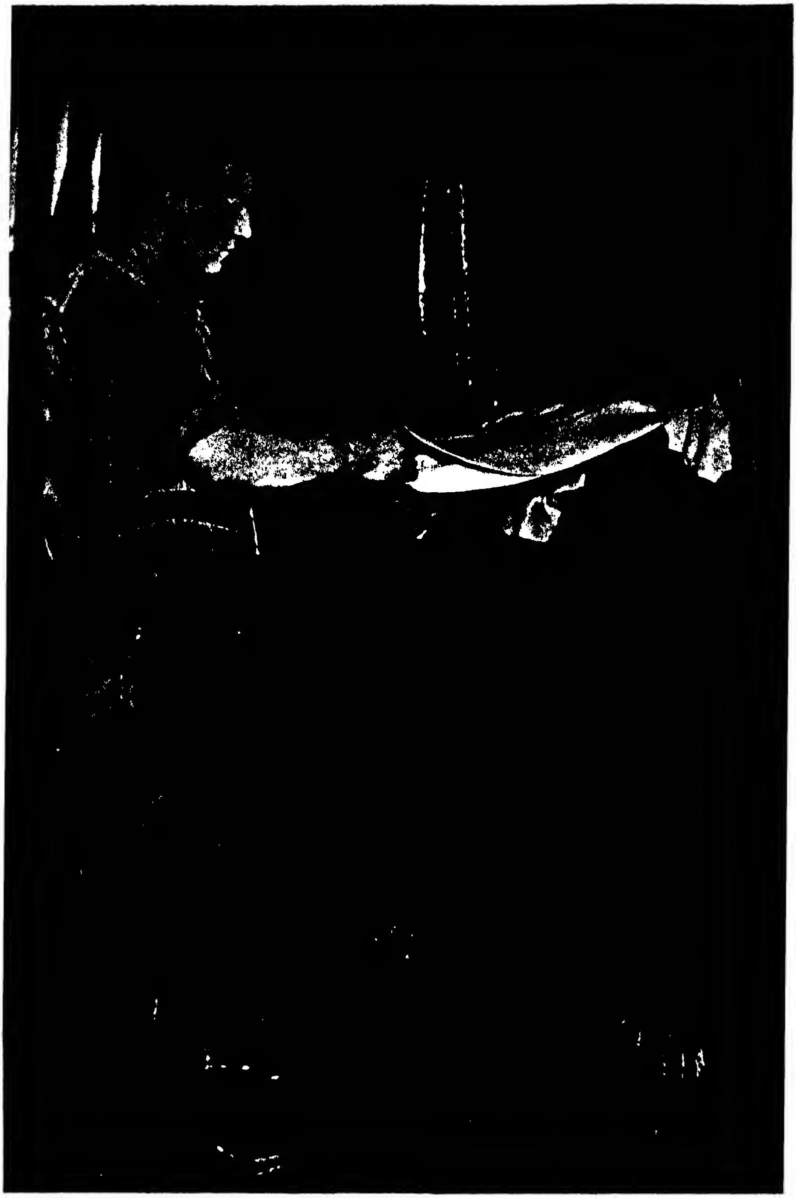
Electrometric Control in the Tannery

The tedious, complicated and lengthy laboratory methods of the academician are no longer acceptable or suitable for the modern and progressive tannery. Laboratory control of today needs to be simple, accurate and quick if it is to be of real value and assistance to the technologist. Ordinary colorimetric or indicator methods are unsuitable for many applications in the tannery owing to the variable and uncertain results obtained. The unreliability of many of these are mainly due to the personal equation in the determination of

masked end points. It should be remembered that the leather chemist is dealing with tinted and coloured liquids which contain dissolved proteins, appreciable percentages of neutral and acid salts, together with other disturbing matter of a colloidal nature. Even improved colorimetric methods of determining pH values such as the capillator used in conjunction with its compensating cell, are only accurate to about 0.2 to 0.3 pH unit when utilized by skilled and experienced workers. The strip method of Wulff (*Koll. Zeitsch, 1926, 40, 341*) is a useful but approximate comparator process. It relies for its accuracy upon the colour sense of the worker and every chemist knows the differences which exist concerning the common recognition of colours even among scientific men.

A few years ago it would have been absurd to have coupled simplicity with the measurement of hydrogen on concentration. The apparatus then available was exceedingly complicated, delicate and required a high degree of technical skill to operate successfully. It was only utilized by the research chemist, and owing to the difficulty and tediousness of manipulation it was by no means popular with the works chemist. Comparatively recently, W. B. Pleass writing from the laboratories of the British Leather Manufacturers' Research association says: "The electrometric methods of determining pH values, although usually of greater accuracy, are not so quick or simple as the colorimetric methods." Fortunately this is now changed and there are on the market instruments for electrometric measurement of pH which are simple to work and certainly quick and reliable.

A new form of meter particularly suitable for use in the tannery incorporates a valve electrometer and is used with a glass electrode. This form of electrode has many advantages; it enables the pH of coloured, turbid or easily reducible liquids or of semi-solids to be accurately measured, and



DRUMMING

GOODS SHOULD BE KEPT UNDER CONSTANT SUPERVISION . . .

in association with the new pH meter forms an easily operated outfit having a wide field of usefulness. A direct reading of pH values is possible as the instrument is calibrated in pH units and therefore requires only limited technical knowledge and few calculations or reference to tables.

There is no doubt that the ease and quickness of routine measurement renders the pH meter of the utmost importance for accurate control of key processes. The instrument can be used by non-scientific men after a very short experience and this relieves the chemist of some of the ordinary routine control work and does away with the necessity for expensive qualified assistants. The pH meter should be used in conjunction with comparative graphs which illustrate the average normal pH values for all liquors at standard temperatures and pressures.

The pH readings for all liquors should be plotted against the age of the liquor to be tested. Thus in the case of a soak, the first test should be carried out with fresh water before the entry of the skins into the pit. Second determination with liquor after eight hours, and further tests carried out every eight hours, or at pre-arranged intervals until goods are unhaired or de-wooled. In order to obtain readings representative of the pH values of a normal soak a large number of tests are necessary. As every tanyard boasts of different methods, it is impossible to do more than suggest the best means of obtaining comparative curves. If a soak is ever used for two or more packs of goods and is then followed by a fresh water soak, it is necessary to adjust the graph accordingly and to carry out a large number of tests. To enable the standard graphs to be trustworthy it is essential that conditions governing these and all subsequent curves are approximately the same. The number of skins per pit or paddle, volume of liquor and temperature must be as constant as practice will allow.

In the case of two or more classes of skins being worked, it is necessary that corresponding numbers of standard graphs should be prepared. The kind of cure and nature of skin, play important parts in determining the extent of bacterial and biochemical action. A graph depicting the variation in pH values of a calf soak will differ considerably from one showing the readings of a goat soak. In the soaking of the latter there is much greater evolution of both ammonia and hydrogen sulphide, than in the case of calf skin. (*E. R. Theis, J. A. L. C. A.* 1930, pp. 442–460.)

The pH readings obtained during the working of test packs should be carefully recorded and filed together with all other relevant data. A good filing system simplifies reference and adds to the general efficiency of the laboratory. A complete and reliable chemical and chemico-physical history of the pack will often reveal possibilities for improvements or the reason why certain defects are prevalent.

In conjunction with the determination of the pH values of liquors, it is important to find out the approximate pH of the skin or hide at various stages of leather manufacture. Simple spot tests with brom-phenol-blue and other suitable indicators will give useful results when carefully carried out. These pH values in conjunction with accurate readings of liquors will be of the utmost value to the chemist and works manager. Many of the problems of modern tanning can be solved by regulating the pH of the skin and the liquor so that optimum concentrations of hydrogen-ions are assured. Even when tanned hide or skin is being fat-liquored after dyeing the pH of the leather determines the successful completion of the operation as is shown by Theis and Hunt. The fastness to wet rubbing of pigment finishes is another recent problem which is now found to be closely related to "effective acidity" of the dyed leather and the pigment solution.

II

TANNING (VEGETABLE AND SYNTHETIC)

THE mechanism of tanning is still imperfectly understood, and yet the theories accounting for the action of vegetable tannins and complex chromium compounds are so numerous and various that they would fill several large books, the majority of which would be unprofitable to study. As fast as one theory is formulated, another takes its place, but there is some reason to suppose that out of this welter of vague, conflicting ideas, there will one day emerge a shadow of a real and practical explanation. No one doubts that it is important to the industry that the process of tanning should be properly understood, but it is somewhat optimistic to expect that a rational explanation will be obtained by sticking new heads on the bodies, often badly decayed, of old theories, which seems to be rather popular at the moment. A few years ago, the fetish of every chemist was pH, which was made to explain everything; today, however, the good old pH has waned very slightly in popularity, and preference is sometimes given to atomic structure and the electron theory of valence. It would be foolish, indeed, to belittle the importance of pH control in tanning today, but, in the writer's opinion, it is still more foolish to regard every new scientific discovery as affording the one and only true explanation of tanning.

A study of technical papers gives one the opinion, perhaps

quite erroneously, that leather chemists are in too much of a hurry to see their experiments and conclusions printed, and unwilling to test them too thoroughly for fear they should not be worth printing. This may be considered a grave injustice to research workers, but every rational minded tanner should be aware that it is not possible to evolve a useful theory in the course of a few months, and that is what a good many chemists are trying to do today. As a basis for an explanation of tanning we must know a great deal more than we do about the structure and chemistry of animal skin, and the synthesis of the tannins. We must, at any rate, be less ready to accept the findings of early workers, and more critical in our outlook. At the present time far too much pressure is put on leather chemists working in tanneries, and research workers in institutions and universities to publish papers. Unfortunately these papers, in England at least, are considered more in the nature of free press publicity for the governing bodies than anything else, and little importance can be attached to the immature findings of their employes. What the industry needs today is more solid spade-work research and less bally-hoo.

For some years now the Procter-Wilson theory of tanning has been considered the "most rational explanation of vegetable tanning" but as John Arthur Wilson himself points out, this only accounts for the action of solutions over the pH range of 5.0 to 2.5, and does not explain the combination of protein and tannin which takes place in alkaline tan liquors where both protein and tannin are negatively charged. The new theory of Wilson's certainly seems to cover more ground and take into account those awkward exceptions from the normal more reasonably than the old Procter-Wilson theory, but there are a number of loose ends which need tying up. It should be remembered that the ionic theory is not by any means universally accepted, or cared to be.

During the last 50 years great strides have been made in the process of tanning and a number of new and important chemicals have been introduced to the industry. The synthetic tanning agents are the most interesting of the new materials, and many of these have a very complex constitution. In some methods of preparation the process is similar to that of synthetic resin manufacture, the phenol and cresol being transformed into sulphonic acids which are condensed with formaldehyde to form a soluble resin. Sulphonated naphthols, salicylic acid and amino derivatives of naphthalene are now being substituted for the simpler phenols, and instead of formaldehyde, acetaldehyde, acetone, benzaldehyde and other aldehydes and ketones are used.

Most of these compounds possess real tanning ability and find important uses in the industry, particularly for adding to the early suspenders in the sole leather tannery. On the Continent use is being found for by-products of the saccharin industry, namely p-toluence sulphonchloride, from which can be produced arylsulphamido-arylsulphonic acids. These have a marked tanning action on skin and appear to offer great possibilities for re-tanning in association with lignin derivatives, or natural tannins. What is really needed in actual practice is a blend of synthetic tans possessing some filling properties, and there seems to be good possibilities for mixtures of synthetics with low tannin content but high non-tan materials. A well blended extract made up on these lines should prove popular with the trade.

The success of the vegetable tanning process depends to a great extent upon the kind of material chosen. It is now widely recognized that only one kind of tannin is seldom sufficient to produce a fully satisfactory leather, and usually two or more have to be employed. Many factors contribute to the suitability of the tannins, for instance oakwood and oak bark, chestnut and myrobalans have a better acid producing

value than quebracho, hemlock, sumac, valonia and some others. Then again, some natural tannins produce a stronger leather than others, and some, particularly the pyrogallols, are associated with good colour. The tanner in his search for the most suitable materials has to answer two important questions before deciding upon a particular tanning material, or mixtures.

1. Is it obtainable in sufficient quantity and at an economic price?
2. Is it suitable when used alone, or does it require the addition of other tannins?

Some natural extracts are very astringent and have to be handled with considerable care to prevent case hardening and grain damage. Where the percentage of non-tans is low, then admixture with other tanning agents high in non-tans is advisable. Almost any type of leather may be produced by blending the tanning materials so as to produce the required characteristics, such as, softness, light colour, smooth grain or weight. A very satisfactory blend for hat lining leather consists of valonia, myrobalans, oakwood and sumac. The addition of tanning sulphonic acids to natural tan has not yet received the attention it deserves, and yet it has been shown that leather tanned with synthetics, or blends of synthetics with natural tannins, is more resistant to acids than straight vegetable tanned leather. It is also worthwhile to consider the importance and usefulness of additives to the tan liquor for increasing the dispersion of the tannins. Bentonite and colloidal clay are two very useful additives, and J. A. Wilson (HIDE AND LEATHER. 90) has shown that chrome calf will take up 5 pounds of the clay to 100 pounds of hide substance, and only lose 7.8 per cent after continuous washing for a period of 24 hours.

Sumac Tanning

A good Sicilian sumac should average about 28 per cent tannin. Other grades vary from 24 per cent upwards, but for light colour and freedom from objectionable impurities, including sand and magnetic iron, the Italian variety appears to be the best. The success of a sumac tannage depends, however, upon other factors besides the quality of the leaf, and the tanner must infuse the sumac in warm, but not hot water; 100 deg. F. is a good average temperature. He must also take care to see that the vat or paddle wheel used for the infusion is scalded out with plenty of boiling water, or treated with powerful disinfectants so as to destroy all ferments and harmful bacteria liable to turn the sweet liquor. This precaution is particularly necessary in warm, thundery weather which seems to favour acid fermentation. If disinfectants are used to sterilize the vessel, care must be taken to wash the latter out well before use so that no trace of the disinfectant is left behind.

The colour of the sumac tanned leather depends to some extent on the condition of the water. Temporary or permanent hardness salts, if present abnormally, are bad as they cause complex calcium tannates to form and stain the leather. If the water is softened, care must be taken to avoid overcorrection and the presence of free alkali which introduces more difficulties. Even a slightly alkaline water will affect the pH of the tannin solution and help to produce a dark coloured and brittle leather. Softening must be controlled from the laboratory, and it is always safer if the pH is determined as part of the daily routine testing.

Although sumac may be used without any acid, it is always advisable to add a small portion of either mineral or organic acid to the fresh liquor. The amount of acid varies

considerably, but ¾ pint of concentrated sulphuric acid is sufficient for 30–40 dozen average sheepskin grains. Twice this amount of organic acid should be used. Formic is the most suitable acid as it helps to produce a nice clean leather, very soft and well fed; it also has a preservative action on the liquor. Salt is necessary to regulate the acid swelling, and about 45 lbs. may be considered sufficient for the same quality of goods.

The usual method of tanning consists first of all in running the green goods in a spent liquor containing 25 lbs. salt for half a day. The small amount of tannin left in this liquor strikes the grain and prepares the skins for immersion in a fairly strong infusion. The goods should not be allowed to remain stationary in the spent liquor otherwise they will "flake" or stain and it is advisable to keep them on the move all the time. A longer period than half a working day is unnecessary as there is not sufficient tannin in the solution to do more than strike the grain. A good plan is to run the green goods in the paddle starting from nine in the morning until 2:30 in the afternoon. By that time the grain will be struck, and the skin in just the right condition for entering the strong pan. The spent liquor can be run off and a fresh infusion made up straight away. In this the goods need processing until six o'clock in the evening when the paddle wheel can be safely stopped. Providing this practice is adopted there is no fear of the goods getting flaked or stained during the night when they lie in a heap on the bottom of the paddle.

A well proved English method of sumac tanning is the following: "The goods are first put into a weak liquor with four buckets of common salt and the wheel run for two hours. The liquor is then run off and the goods drawn. Hot water is run in and the wheel three-quarters filled with warm water 100 deg. F. Five buckets of common salt then added,

also 1 pint sulphuric acid and 4½ bags of sumac, approximately, 6¾ cwts. The wheel contains 1,500 gallons and processes an average 45 dozen sheepskin grains. Average time of running about 4–5 hours per working day for 3 days or more according to the goods."

HAND-SETTING OF VEGETABLE TANNED KIPS. . . .

Instead of starting the goods in a cold spent liquor, some authorities recommend a warm liquor, 98 deg. F., but the author has not found that this has produced any marked improvement in the leather and introduces some trouble in warming up the liquor. Apart from the straight use of sumac, it may be used in conjunction with other tannins,

particularly myrobalans and gambier. In the manufacture of extra thin skivers, "fly wings" or "bat wings" as they are called, it is an advantage to use a mixture of sumac, gambier and oatmeal, the latter has a valuable filling action. Another good method is to use colloidal clay with the sumac, and thus, also, helps to fill up the "pin holes."

The writer has made some very nice leather by combining sumac with formaldehyde, and after ten years this leather does not show the slightest sign of deterioration, such as loss of tensile strength, etc. The pickled skins were depickled with borax in the usual way, then drummed in a weak formalin solution containing 750 c.c. formalin, 200 c.c. (1 c.c. = 15½ drops), sulphonated castor oil per dozen skins for 5 hours. They were then allowed to remain in the liquor overnight, and next morning drummed in a liquor made up with 8 lbs. sumac and 2 lbs. oatmeal, water 98 deg. F. After a day's drumming they were allowed to remain in the liquor overnight, re-drummed for 4 hours the next day, then washed-up in warm water, allowed to drain for 24 hours, then dried in the open air. The finished leather was delightfully soft and dyed well with acid dyes. It was finished with cellulose spray paints and used for motor clothing.

Apart from the use of sumac with natural tannins and also formaldehyde, it may be used for finishing off and improving the handle and colour of synthetic tanned leather. A combination, synthetic and sumac tanned leather will dye easier and more successfully than a straight synthetic leather. The writer has obtained amazingly good results by first tanning roans with a good sulphonic acid tanning solution and then processing the goods in spent sumac liquor for four days. The non-tans present in the spent liquor were no doubt responsible for excellent handle and appearance of the finished leather which was very plump and soft. There is no reason why instead of using water for making up the syn-

thetic tan solution, spent sumac liquor should not be used as quite apart from the presence of small amounts of tannin and also non-tans, the free particles of sumac have a very beneficial action on the leather. So far very little work has been done along these lines, but the idea seems well worth developing. Sulphited cellulose liquors, especially the soda-base extracts, blend well with sumac.

Sumac Goat

The old bag method of tanning goatskins for bookbinding, upholstery and other high class work is still unequalled, but owing to the high cost of labor, this method is but seldom practiced. It is, however, of interest to consider it for a moment. The skins are made into bags, grain side outside, by means of a strong sewing machine. A hole is left near the tail for the insertion of a large enamel funnel. The bags are almost filled with strong, warm sumac liquor (100 deg. F.) and then blown up and sealed. They are then thrown into a large tub of weak sumac liquor and moved about by means of long poles. The inflated bags float quite easily on the liquor and tanning proceeds very rapidly—in fact, two to three days is sufficient time for very heavy goatskins. The success of the process depends to a great extent upon the way the laborers keep the bags continually on the roll. If the bags are allowed to remain stationary, particularly at the commencement of tanning, there is a risk of serious stains and uneven penetration of the tannin. Three to five hours continual agitation is needed each day.

Half way through the process, the old liquor is run out of the bags and new liquor substituted. When tannage is complete, the goods improve by laying away in sumac for a couple of days to feed.

Although there is no leather quite so good as the genuine

bag morocco, it is possible to produce excellent leather by using either drums or paddles. In the case of the finest quality sumac goatskins, a thorough puering is essential and contributes a great deal to the softness and good handle of the leather. Dog manure is really the best bate, but if artificial bate is used, then the drenching should be carried out very completely. The goods should not be pickled, and after drenching they will need a weak acid treatment in a bath of two per cent lactic for 20 minutes or so. This can be carried out in drum or paddle, preferably the former. Tanning should be commenced in a spent tan and proceed as described for sheep grains. It is, however, advisable to use warm liquors for goatskins and a higher temperature may be safely employed than is customary for sheepskins. There is no need to add salt to the sumac liquor, but the addition of half the normal quantity of organic acid is useful. After processing in sumac liquor sufficiently long to tan, some tanners lay the skins down in a strong infusion of sumac and leave them for three days or so. This certainly helps to produce a superior kind of leather and can be recommended.

Sumac for Retanning

This natural tanning material is widely used in the light leather industry both for retanning and improving the color and handle of crust leathers, particularly those of Eastern origin, such as East India tanned sheepskins. Procedure varies a good deal, but a common practice in England is to wash the crust leather to remove the surface filth, then to strip the goods slightly with a mild alkali to remove loose tannin and grease. After drumming in the alkaline solution, ½ per cent borax on crust weight being quite usual, the goods are then well washed with plenty of cold water, and acidified by a further drumming for 15 minutes with ½ per

cent sulphuric acid, or ¾ per cent formic, so that the leather gives an acid reaction before retanning. This is carried out with sumac infused with warm water 100 deg. F. for half to three quarters of an hour. Afterwards the goods are rinsed in a tank of cold water and horsed up for 12 hours before further processing.

In the case of natural shoe linings, the retanning may be a mixture of sumac and a sulphonic acid tanning agent, or sumac and a good soda-base cellulose extract. The latter blend is very economical and satisfactory as it produces a very light leather possessing a nice feel. Tanners who use synthetic tanning materials invariably finish off by a short processing with sumac which adds a good deal of weight to the otherwise rather empty leather.

If desired, colloidal clay, oatmeal and sulphonated oils may all be usefully added to the sumac liquor to produce certain effects. The addition of oatmeal greatly improves the appearance and feel of poor grains and helps to feed them up. For natural shoe linings, the addition of colloidal clay is to be recommended, especially if used with sulphonated castor or olive oil.

On the completion of some vegetable tanning processes, especially those where quebracho and other dark colored tannins are employed, it is customary to finish off the goods with a run in warm sumac liquor, which always improves the color of the finished leather. The sumac appears to have a dissolving action on some of the dark coloring matters found in catechol tannins.

Sumac Mordanting

The leaf infusion, or the extract, is excellent for mordanting chrome tanned leathers, and useful proportions consist of 1½ pounds of high tanning sumac, or ¾ pound good

sumac extract, per dozen skins. The temperature of the liquor should not exceed 120 deg. F. Drumming is the best way of processing the goods and penetration is assured in half or three-quarters of an hour. Flemming recommends the use of titanium-potassium oxalate, 4 ozs. per 100 lbs. leather, as an addition to the sumac mordant, and this is to be recommended.

Sumac can be usefully combined with other mordants, such as fustic, peachwood and gambier, but for very light, clean shades of color, sumac extract should be used alone, or in conjunction with titanium. Although basic dyes are usually employed alone for dyeing chrome tanned leather, some tanners like to combine them with direct cotton colors, and where this practice is followed, sumac will be found very advantageous for preliminary mordanting. The dyeing should be carried out in the exhausted but warmed-up mordant bath.

A preliminary mordanting with sumac greatly improves the evenness and penetration of acid dyestuffs, and is particularly usefül in those cases where pigment finishes are not to be used and where an exceptionally fine, clean colored grain surface is imperative for the best results.

Advantage of Adding Organic Acids to Sumac Tanning Liquors

Although it is a common practice to add sulphuric acid to the sumac liquor to induce some swelling, this effect is better produced by the addition of safe organic acids. Apart from the grave danger of the finished leather being destroyed as the result of acid corrosion, the addition of sulphuric acid has a tendency to reduce the buffer index of the tan solution and thereby lower the reserve of acid. According to Winifred B. Pleass (J. S. L. T. C. Feb. 1931), "additions of small

quantities of sulphuric acid to a mellow liquor will reduce the buffer index of the liquor, usually without appreciably altering the pH value." The acid does, however, react with the soluble calcium salts of weak acids, which act as buffers, and form a precipitate of calcium sulphate. This is liable to cause trouble if it is precipitated in the pores of the skins. Greater additions of sulphuric acid to the tan liquor reduce both the pH value and the buffer index figure, whereas the addition of a weak acid, such as lactic, increases the buffer index figure. Winnifred B. Pleass points out that, "unlike sulphuric acid, large quantities of lactic acid will not reduce the pH figure much below 2.7, but further additions continue to increase the buffer index." As a low buffer index means a firm and solid leather, it is desirable to have an average buffer index of 4 for tan liquors built up of sumac.

Corrosive Properties of Sumac

Next to sulphonic acid tanning materials, sumac has the most corrosive effect on metal-work, and it is necessary to protect metal parts in some way so that they will not be subject to continuous attack. Stainless steel, preferably one containing high percentages of both chromium and nickel, resists the action of the tannins better than ordinary steel or iron. Nickel alloys, such as Monel metal, are also recommended.

Gambier

This usually reaches the tanner in the form of large blocks weighing round about 250 lbs. and containing 35 to 40 per cent light colored tannin, which Procter says is a catechol phloroglucol derivative. The small cubes of better class gambier contain a higher percentage of tannin than is present in the larger blocks, and may even exceed 65 per cent.

The small cubes are not generally used for tanning, but find ready application for mordanting and other dyehouse purposes.

Gambier is a most important tanning material, but a straight gambier tanned leather is inclined to be very spongy and soft, and for this reason it is frequently blended with other tannins, some of which are more economical for general use. Sumac, oakwood, quebracho, chestnut, valonia, etc., can all be used with gambier. It also blends perfectly with alum and salt to produce a smooth, soft and exceptionally fine leather. The famous Dongola leather is made by tanning calfskins with gambier, alum and salt and well stuffing with egg yolk, neatsfoot oil and other fatty materials. Alum is sometimes used for clearing the grain of gambier tanned leathers and appears to have a beneficial effect. Gambier leather can be retanned with basic chrome salts to produce a superior and very soft semi-chrome leather suitable for gloving and clothing purposes. From experiments recently undertaken it also appears that gambier blends with synthetic tanning agents, including sulphite cellulose waste liquors.

In the case of the straight gambier and salt tannage, the best procedure is to start the pickled goods in a paddle containing a weak liquor just strong enough to strike the grain. Flemming recommends a barkometer strength of 12 degrees, but the author considers that 8 or 10 is safer when it is desired to produce an exceptionally smooth grained leather. It is advisable to use a spent liquor in preference to a new one, even if the former shows a higher barkometer strength than the latter. As all tanners know, spent liquors are very mild in their action, probably due to the high percentage of non-tans and organic acids present. A good plan is to start the tanning in a spent liquor and when the grain has struck, to run off the liquor and use a fresh one. Some tanners consider it necessary to depickle the goods before tanning, but

this always seems hardly worthwhile, especially as it has a tendency to render the fibres rather tender. Instead of depickling, a better plan is to take goods straight from the bran drench, or even from the puer provided they have been well washed. When dealing with pickled goods kept in store for several weeks, a preliminary drumming in salt solution, 10–15 per cent, is advisable to work out the creases.

Drum, rocker and paddle can all be used for gambier tannage, but the paddle seems the most suitable. Rather more salt is necessary when gambier is used alone than is required if other tannins are used. Acetic, lactic or formic should be added to the tan liquor to prevent the goods from being too thin and empty.

A good working recipe for calfskins is the following: commence tanning in a paddle containing spent gambier liquor, 10 degrees barkometer strength, and two large pailfuls of rock salt. Work the goods until the grain is colored then draw them and run off the liquor. Make up a fresh gambier solution so that the barkometer strength is 20 degrees with four pailfuls of salt and one quart of lactic or formic acid, preferably the latter. Run the goods for three days, then increase the strength of the liquor to 30 and process until thoroughly tanned.

After tanning, the goods should always be horsed up for at least a day—two if convenient, then drummed in a warm infusion of sumac and a little sulphonated castor or olive oil. For fifteen dozen calfskins, about 40 lbs. sumac and 4 lbs. sulphonated oil will be found useful proportions. Although this re-tanning renders the total cost greater, the leather is considerably improved and has a better handle. Instead of sumac, some tanners use sumac extract and some use oakwood extract. Both of these are to be recommended, but the ground leaf sumac is to be preferred. Oatmeal has a filling action and is a good additive to all gambier tanning liquors.

Planning the Combination Tannage

It is an astonishing fact that comparatively few tanners appreciate the full possibilities of combination tannages, and how it is possible to alter the characteristics of the finished leather by simple changes in the composition of the tanning mixture. Such tannins as sumac, myrobalans, gambier, pine bark and chestnut give fairly soft leathers, whereas, oakwood, oak, quebracho, valonia and mimosa yield firm to medium leathers. It is, however, not only the tannins themselves that influence the character of the leather, but also the non-tans present. F. Stather and H. Herfield (*Collegium*, 1935, 463–470) found that the thickness of the tanned leather can be greatly improved by increasing the proportion of non-tans present. A high non-tan tanning solution also improved the water absorption properties of the leather, and the ease with which it could be wetted back from the crust.

To produce a well-balanced leather suitable for a particular purpose, such as gloving, shoe linings, uppers or clothing, the tanner has to find the best and most economic blend of tanning materials, supposing, of course, that he uses a vegetable tanning process. The question of price is all important and he must be prepared at short notice to substitute cheap tannins for expensive ones, and yet not affect the quality or appearance of the finished leather. This is difficult, but by no means impossible. A great deal can be done to discover the best commercial blends of extracts by practical experiments in the model tannery. By bringing the changes on about the various tanning materials it should be possible to work out suitable combinations, but the experiments, to be valuable, must be very carefully carried out at regulated pH and buffer index figures. The scientific approach to this practical problem cannot but prove of the great value to the

tanner, and enable him to be always in the position to make changes in the tannery with the knowledge and confidence that they will be successful in works practice.

A number of important factors have to be taken into consideration when planning a combination tannage. It is not only a matter of producing a leather soft enough for the purpose, but one possessing the proper tensile strength, elasticity, fineness of grain and affinity for coal tar dyes, all of which can be influenced by the choice of tannins, and the conditions under which they are employed in solution.

Gambier Combination Tannages

Gambier and Sumac

This is a somewhat expensive, but nevertheless excellent tannage when it is desired to produce an exceptionally soft leather of good light color and high affinity for acid dyes. The best practice appears to be to half-tan the goods with gambier and salt liquors as described for a straight gambier leather. Starting first with spent liquor, the strength of the new liquor should be gradually increased until 25 degrees barkometer strength is reached. After three to five days paddle work, or less time slow drumming or rocking, the goods should be allowed to drain for a day. Slow draining is more beneficial than hydro-extracting, but when it is necessary to quicken-up the tannage, then the latter may be usefully employed. The sumac liquor should be made by infusing 100 lbs. of best ground sumac leaf in a paddle three-quarters full of warm water, 100° F. and containing two pailfuls of salt and one pint of formic acid. The goods need running in this liquor for two days, or until thoroughly tanned. If the goods are not in the pickled state when they pass into the gambier liquor, the latter should be acidified with half again as much acid so as to obtain a reasonably plump leather.

Gambier Drum Tannage for Fine Leathers

A mixture of gambier, myrobalans, quebracho and valonia can be used to produce a high quality leather specially suitable for hat linings. The method is as follows:

The sheepskins, or calfskins, are taken from the drench, or puer, and drummed in a weak solution of acetic acid 40 per cent strength, for 20 dozen sheepskins, about 1,500 ccs. needed. After a run of ten minutes, the goods should be taken out of the drum and drained. A liquor consisting of 5 grms., tannin per litre should be made up in the drum together with half a gallon of light mineral oil to reduce the surface tension. The tanning material used should consist of the following mixture:

125 lbs. gambier.
50 lbs. myrobalans extract.
85 lbs. quebracho extract.
40 lbs. sumac extract.
65 lbs. valonia extracted with hot water.
200 gallons of water.

This stock solution contains a nice blend of tannin and should be used to strengthen the weak liquor in the drum at the rate of 4 gallons every 2 working hours throughout the day. When tanning is complete, the goods require horsing up for a day then drumming in warm sumac liquor containing sulphonated castor oil.

Gambier Tannage for Modeling Calf

When it is desired to produce a calfskin leather with a very fine, smooth grain, the author has found that useful results can be obtained by painting the skins on the flesh side with tannin solutions rich in gambier. One advantage of this method is that tanning takes only a short time, three days being sufficient for large calfskins.

The best solution is made by dissolving 50 lbs. gambier, 25 lbs. sumac extract, 25 lbs. myrobalans extract, 10 lbs.

quebracho extract and 5 lbs. oakwood extract in 75 gallons of water and adding to this 15 lbs. turkey red oil.

Pickled skins are the best for this method of quick tanning, and they should be drummed in 15 per cent salt for 20 minutes before painting. After painting on the flesh, the skins should be placed grain to grain in small heaps. Too much liquor should not be given at first; in fact, all that is necessary is to apply as much tan liquor as the skin substance can soak up in a few minutes. Painting should take place every one and a half hours until the goods are tanned. They then need drumming in a warm and strong infusion of sumac to clear the grain and give it a good finish. If the skins are coated on the grain with a light mineral oil before painting they have a less tendency to show any signs of grain contraction.

Gambier, Quebracho and Myrobalans

This is a popular commercial formula for tanning sheepskins, and by varying the proportions of the three tanning materials it is possible to alter the character of the crust leather to a considerable degree.

A rough basil tannage that produces a good leather is the following:

Drum 45 dozen pickled sheepskins in 10–15 per cent salt solution in a drum for 20 minutes. Drain the goods and transfer them to a paddle wheel, capacity 1,200 to 1,500 gallons, containing a weak solution of mixed tannins, equal proportions of gambier, quebracho extract and myrobalans extract, and with a strength of 7 grms. tannin per litre of solution ready for use. The wheel should contain 4 buckets of common salt to reduce swelling. After a week's slow running in the paddle, motion being reduced to four hours daily, the goods should be passed into another paddle wheel containing 15 grms. per litre of mixed tannins. After three days in this liquor, the goods will usually be thoroughly tanned,

but it is advisable always to test cuttings in the laboratory with glacial acetic acid which will show the penetration of the tannin. No salt is needed in the last liquor, and it is also unnecessary to add acid.

To reduce the cost of the tannage, and also to obtain a slightly firmer leather, the proportions of the three tanning materials can be altered so that only half the quantity of gambier is used, extra amounts of the other extracts being used.

The addition of oakwood extract increases the firmness of all gambier leathers and is sometimes exceedingly useful.

Gambier and Alum

The ordinary combination tannage described above is not always suitable when the goods are to be chromed, and a better, quicker and more economical method is to use an alum and gambier tannage. This is very simple. Drum the goods in salt liquor, 15 per cent, for 20 minutes, then drum or rock the goods in the following liquor:

350 gallons water.
60 lbs. alum.
45 lbs. gambier (sufficient to tan 40 dozens).
30 lbs. salt.

Three days should be sufficient to tan the goods, and they should then be horsed up for a day, then hung up to dry in slightly warm shed.

In some cases it may be desirable to take goods straight from the bran drench, or puer, instead of from the pickle, and for gloving leathers this method is to be preferred. The alum and gambier combination tannage is to be recommended for fly wing skivers intended for piano work. The goods can be processed in almost the same way as described above, only for these goods, it is necessary to feed with oatmeal and colloidal clay, or bentonite. The oatmeal should be mixed with lukewarm water not exceeding 98° F., otherwise it be-

comes cooked. Both clay and oatmeal have a very beneficial effect on the leather, and also fill up the objectionable pin-holes so often found with these extra thin splits. After tanning, the grains should be dried out in a cool shed, perched on the split side, brushed, ironed and examined for pin-holes. If these are still present, then the goods must be wet down and fed-up with more oatmeal and colloidal clay. Ordinary clay is of no use, and only the finest colloidal variety should be used.

Quebracho Extract

This highly concentrated and difficulty soluble tannin has its origin in South America where the iron trees are felled, chopped and prepared for export to various parts of the world where they are extracted. Solid quebracho extract reaches the tanner in two forms, first the normal extract containing a high percentage of insoluble matter (6 to 10 per cent), second, the sulphited extract with no insoluble matter and a higher percentage of non-tans, 14 per cent instead of 7 per cent. The tannin content is usually about 66 per cent for good quality extracts. The very small percentage of non-tans in the untreated extract is responsible for the astringency of the tanning solutions, and the firmness and brittleness of the leather. For this reason, untreated quebracho, and even the sulphited extract is seldom used alone, but nearly always in conjunction with myrobalans, gambier, etc.

The unsulphited extract requires to be boiled continuously with water before use, and even then, the dark, heavy, resinous precipitate is not absorbed by the solution. Strangely enough, the insoluble matter, which is rich in tannin, is slowly absorbed by the pelt and never wasted. The absorption of insoluble, or difficulty soluble tannins is, however, a good deal slower than is the case of tannins in solution.

Procter points out that the addition of alum to the quebracho liquor greatly improves both the color and quality of the leather, and the author has found that this works out very well in practice. It is a good plan to use a blend of quebracho, gambier and alum and to finish off by a run in warm sumac, which greatly improves the handle of the leather and lightens the color. When using quebracho as an important ingredient of the combination tannage, it is essential that the other materials should be rich in non-tans and that organic acids be used to plump up the goods. The tendency of quebracho is to produce a thin, hard leather, and therefore the tanner must use it with a certain amount of care. It is a valuable tannin, and properly used can be of the utmost commercial value. Goods to be tanned in quebracho liquors should be in the swollen pickled state and never taken straight from the drench. For linings and cheap basils there is no better tannage than quebracho and myrobalans, using two pounds of myrobalans extract to one pound of sulphited quebracho extract. The paddle is the best vessel for tanning, and a week's slow running should be sufficient, starting in a spent liquor about 5 grms. per litre tannin, and working up by easy stages to a 17 grms. per litre liquor. Gradual strengthening of the tan liquors is most important as considerable damage is done by using liquors too strong for the condition of the goods. The addition of salt, 50 lbs. to the paddle wheel is an advantage, and it also pays to use a quart of lactic acid for each pack of goods. At the completion of the tannage, the goods derive great benefit from laying away in sumac liquor, or drumming in a warm infusion.

This is one of the most useful tanning agents, as it is not only very economical in use, but readily adaptable and suitable for a number of different purposes. Owing to the astringency of the tannin, and the low compensating value of the non-tans, quebracho is generally used in conjunction with

other tanning agents, particularly those of an acid producing nature. Quebracho is used most successfully when the skins are in a well-plumped condition, otherwise there is always a danger of "case-hardening." In conjunction with myrobalans, gambier, hemlock and certain synthetic and cellulose extracts, quebracho forms excellent tanning mixtures, not only for complete tannages, but also for re-tanning.

The most usual form of quebracho is the solid extract,

ENGLISH TANNERY DRUM

USED FOR TANNING SHEEPSKINS . . .

which contains from 63–67 per cent tannin. The bulk of the tannin is extracted from the heartwood, and according to Paessler, this shows an analysis of:

17.5% tannin.
2.5% soluble non-tans.
65.5% insoluble matter.
14.5% moisture.

The natural quebracho extract is difficulty soluble, and it requires continual boiling for several days to dissolve it thoroughly; even then, it is liable to be thrown out of solution by dilution, or a sudden drop in temperature.

Flemming in his extremely useful book *Practical Tanning* says: "Solid extract needs to be boiled up in hot water in a tub containing a false screen bottom which prevents its adhering to a solid surface. The liquid extract should be dissolved in water at 180° F."

The dark colored precipitate, or sludge, frequently formed when quebracho extract is poured into cold tan liquors, is not just insoluble matter, but consists mostly of phlobaphenes, and other complex tannin bodies. These have the power of tanning hide substance, and are absorbed during drum tannage.

A certain amount of sulphited quebracho extract is used in light leather tanneries. This form of quebracho, which is fairly readily soluble, is due largely to the work of Dr. Lepetit. Apparently, the autoclave treatment of quebracho with bisulphites results in certain radical chemical changes, and the resulting extract differs in many ways from the natural product. Although producing a lighter colored leather, the sulphited extract has a tendency to harden the grain and render the leather somewhat harsher. In conjunction with acid producing tannins, sulphited quebracho will, however, produce excellent leather. Experience with this form of quebracho indicates that unusual care needs to be exercised in the choice of tannin additives. The addition of alum to both natural and sulphited extracts of quebracho, particularly the latter, results in increased softness and a better color.

A factor which often influences the success, or otherwise of quebracho tanning, is the presence of small amounts of lime in the skins, or in the water used for leaching. All

skins to be tanned in tan liquors containing any large proportion of quebracho should be well pickled, either with formic acid and salt, or the more usual vitriol and salt. The water used for dissolving the extract, or making up the diluted liquors should be freed from lime by carefully controlled softening. Alternatively, the water may be obtained from a natural well or spring. Lime not only gives the tanned leather a bad color, but tends to make the grain rather brittle.

The writer has found that the addition of lactic, acetic, and formic acid, preferably lactic, to the quebracho liquor during the early stages of tanning helps considerably to produce a well-filled and satisfactory leather. The addition of one of these organic acids can, of course, be chemically controlled by the usual Comparator Method, so as to maintain a pH round about 3.5, or at a figure found by the tanner to be most satisfactory for his particular class of goods.

An interesting side-light on the respective values of natural and sulphited quebracho extracts, as regards their true tanning fixative values, is given by F. Stather and R. Lauffman, *Coll* (1935, 420). These two chemists carried out a number of experiments with strips of cold-air dried corium prepared from butt pieces of cowhide. They soaked back the strips and tanned them with various extracts at their natural pH values, using 200 per cent tannin on the air dried weight of skin. The tannin concentration was gradually raised during the course of four days from 0.4 per cent to about 7 per cent and tannage continued for 64 days. Portions of leather were taken away at intervals, washed, air-dried, analyzed and the degree of tannage calculated and plotted against time. The curves were found to rise rapidly at first up to eight days, and then flatten out. After 16 days, about 75 per cent of the maximum is fixed with oak, and pine barks, 80–85 per cent with sulphited quebracho, valonia,

myrobalans and gambier, and over 90 per cent with ordinary quebracho, chestnut, mimosa, sumac. The curves eventually intersected so that the order of the materials as regards the degree of tannage alters with time. According to Stather and Lauffman, the amounts of the irreversibly fixed tannin after 64 days were, pine bark, 30.5; sumac, 40.9; oak bark, 41.8; gambier, 42.1; valonia, 45.6; chestnut, 46.2; myrabolans, 51.3; mimosa, 51.9; sulphited quebracho, 52.2 and natural quebracho, 53.3 (per 100 parts hide substance).

In works practice, it is generally found that natural quebracho extract has a greater tanning fixative value than the sulphited extract, and for this reason, the former appears to be more suitable for most light tannages, whereas, sulphited extract, on account of its greater solubility and good color, can be recommended for all re-tannages.

The writer has found that colloidal clay is most valuable as a filling agent for pure quebracho tannages, and the addition of 2–3 per cent of the weight extract has a most beneficial effect. European tanners seldom exploit colloidal clay as fully as it deserves, but it can be recommended for most vegetable tanning processes, especially quick drum tannages.

Oakwood Extract

This is another sole-tanning extract, somewhat lower in tannin than chestnut, approximately 25–28 per cent tannin. The true oakwood extract, to be distinguished from mixtures of low grade chestnut and quebracho, does not blend as easily as chestnut, and is therefore, not of such great use to the light leather tanner.

The writer has found oakwood of service for re-tanning case leathers, also for blending with other extracts when tanning calf and light hides for semi-chroming. It does not, however, appear to be very suitable for either sheep

or calf, and there is no reason why it should be used for goatskins.

Oakwood appears to have a tightening action on the grain, and although it is sometimes useful to correct any looseness by the addition of oakwood to other blends of extracts, it must always be treated with certain amount of care.

Now that oakwood is fairly cheap, a very profitable avenue for its use in the tannery appears to be in conjunction with synthetic tanning agents, also with sulphited cellulose extracts. When used with these it helps to produce a well filled leather of a distinctly superior character.

Hemlock

Although this extract is produced in considerable quantities in America and Canada, it does not find a very great use in Europe. The tannin value of hemlock barks varies considerably according to the locality, thus in Washington the bark may be just over 11 per cent, whereas in other parts of the country, the tannin content may barely reach 9 per cent. The extract also varies, but 25 per cent is a fair average.

Hemlock bark extract is used to a considerable extent for tanning sheepskins intended for fancy leather and shoe linings. The process is generally carried out in a drum, and first of all, the pickled goods are run in a 5 per cent salt solution before being thrown into the tan liquor. This consists of very weak fresh hemlock, or better still, spent liquor. About 2 per cent salt needs to be present in the first liquors to prevent undue swelling. When the color has struck, and the goods in a "settled" condition, they are immediately transferred to a sweet hemlock liquor, about six barkometer strength, and slowly drummed until tanned. Periodic feeding with fresh liquor, about every

three hours, should bring the barkometer strength up to 12 when the goods are three-quarters tanned. After complete tannage, the skins are best laid away in fairly strong hemlock, 25 barkometer strength, for 24–48 hours, then washed up in a weak and warm sumac liquor.

If the hemlock is used in conjunction with quebracho, a slightly superior leather is made.

Chestnut Extract

This extract contains an average of 30 per cent tannin, and according to Procter, the important tannin constituent strongly resembles oakwood and divi-divi. The tanning material is far more important to the sole leather tanner than to the light leather manufacturer, but it has always found a certain amount of favor for blending with quebracho, hemlock, myrobalans and other extracts. During recent years, chestnut extract has greatly increased in popularity with light leather tanners.

In some ways, chestnut strongly resembles quebracho, especially as regards solubility in cold water, and sensitivity to free lime, either in the water, or the skins.

The writer has found that when using chestnut extract alone in the early stages of tanning light skins, there is always a risk of tanning stains, especially on calf and roans. When chestnut is to be used, it appears to be most satisfactory to use it toward the end of the tanning process, and to start tanning with a very mellow blend of mixed extracts. Chestnut extract is an excellent filling material, hence its great popularity with sole leather tanners, and it should be of the greatest service to the light leather industry provided it is carefully exploited.

There is a considerable difference between the various chestnut extracts now on the market, and the tanner should

pay particular attention not only to the percentage of tannin, but also the color value, and above all, its ability to produce the right kind of leather at an economical price. Buying on analysis is, of course, a safe and excellent method, but a good analysis is not always certain proof that the extract will meet with requirements. The tanner will be well advised to valuate an extract on both practical and laboratory tests; both are inseparably related. Once an extract, or blend of extracts has been found to give satisfaction, then every effort should be made to keep to this and so standardize the tanning process. It will certainly not pay the tanner to change brands for the sake of a little extra tannin, or perhaps improved coloring. The writer has more than a suspicion that intensive decolorization and purification often do more harm than good.

Chestnut produces a well filled, that is, rather firm leather, and while it should be present in most blends, it must needs be used with rather more care than some of the other extracts, such as myrobalans. This extract blends well with chestnut, and so also does quebracho.

When chestnut is used alone, the tanned leather is rendered more sensitive to coal tar dyes, and has both an improved handle and better color, if well drummed in warm sumac liquor containing ½ per cent sulphonated olive oil.

Flemming gives the following method of tanning sheepskins with chestnut extract: "Sheepskins, prepared as for any other tannage, may be tanned by being hung in chestnut liquor or drummed in liquor made direct from the extract, or from a mixture of chestnut and quebracho extracts. If the skins are intended to be colored after they are tanned, it is best to tan them direct in the extract liquor and then to retan them with sumac. Stock to be run in the natural color is usually struck in the combination liquor giving the shade desired. With very thin skins the main requirements

of the tanning material is that it is clean, bright and quick in action. Tanning can be begun in a paddle and finished in a drum, the leather being then dried, treated with sumac, colored, fat-liquored with acid fat-liquor, and dried and finished."

The writer considers that an improvement on this method would result if the skins were first struck-through in a weak, or perhaps spent solution of quebracho and myrobalans, containing ½ per cent lactic acid, but no salt. Both calf and roans will work quite well this way if taken direct from a bran drench. If the goods are taken from the pickle, then 1½ per cent salt is necessary to reduce acid swelling. After striking through, the old liquor can be run off, and a fresh, sweet, chestnut solution made up. It helps considerably during the early stages of chestnut extract if the temperature of the liquor is about bloodheat.

Divi-divi

This Central American tannin is used to a large extent in the heavy leather tannery, and does not find many applications in the tanning of light leathers. Although possessing a high tannin content, the dried pods, 40–45 per cent pyrogallol tannin, which Procter says is mainly ellagitannic acid, and many of the characteristics of a valuable tanning agent, it is not particularly popular. The reason is that the solutions are liable to ferment, and tanned leather to assume an objectionable reddish color rather difficult to cover. The addition of synthetic tannins to divi-divi helps materially to reduce the risk of fermentation owing to the preservative action of the sulphonic acids. Weak organic acids and their salts are also useful in this connection, especially lactic. Procter recommends divi-divi for drum tanning, and states that an excellent color may be produced.

There are several other tannins similar to divi-divi, but they have not yet received serious recognition.

Mimosa

This is a useful catechol tanning material for the sole leather tanner, but of limited use for the light leather dresser who has available a number of other tannins more suitable for his purpose, which is to obtain a light, full leather at a purposeful price.

Spruce

Although spruce and super-spruce extracts are used to a large degree in the States, they do not find many applications in the English tannery. The writer's experience of spruce extracts is that they are particularly valuable for blending with extracts low in non-tannins and fermentable sugars. Addition of lactic or other weak organic acid to spruce liquors is recommended, and some tanners are now using sodium acetate to control the pH so that uniform results can be obtained. Spruce blends well with certain synthetic tannins, and when used with tans similar to Ordoval, a nice, full, smooth grained leather is obtained, the color being light and clean. Very similar in action to American spruce are the various larch tans used in Scotland for processing basils. When properly used, these materials will produce good class, strong leathers, but they are not so economical in use as modern extracts.

Many tanning materials have not been mentioned in this brief survey, the purpose of which is to describe the practical value of the most important tannins. So many tannins are of purely local interest, and although, perhaps, very important in one district, may be practically unknown in others.

Every year sees the introduction of some new and interesting tannins, but the majority of these are of academic interest only.

III

SYNTHETIC TANNING MATERIALS

SINCE the experimental days of Stiasny's Neradol, great progress has been made in the production of syntans.

There are today very few tanneries, either in America or Europe, where synthetic materials are not used. Sometimes they find employment for complete tannage, but more often they are used to supplement vegetable, mineral and formaldehyde tannages. Apart, however, from their use as tanning agents, certain of these chemical bodies find important applications in the bleaching of both chrome and vegetable leathers. They are also used for tightening the grain of naturally loose skins and for filling the empty shanks of low grade side leathers. In the United States, particularly, great progress has been made in bleaching chrome leathers with various syntans, using simple mixtures of basic chromium salts and synthetic tannins for tanning, or processing the fully chromed leather in liquors made up of syntan, sulphonated oil and white pigment, usually titanium oxide because of its great covering power. A few high priced synthetic agents are of great value as mordants when dyeing chrome leathers light, delicate shades.

Whereas 10 years ago the tanner progressive enough to use synthetic tanning material bought an old barrel or so of cheap syntan, usually very acid, which he used for crude bleaching, or perhaps filling purposes, today he buys several

different varieties. Although one brand may be excellent for bleaching, it might not be suitable, or economical for re-tanning. It quite often happens that syntans good for tanning sheepskins, are little use for mordanting. The production of these chemical bodies is now on a highly specialized basis, and each particular product is recommended for a special purpose. There are, of course, synthetic tanning materials which can be used for several different jobs, but usually this is not economical, and it pays to buy for a particular process. Apparently this is rather expensive, but in works practice it is cheaper in the long run.

The difficulties experienced by the tanners who first used Neradol D. have now been completely overcome. With reference to the latter, Grasser in his book on *Synthetic Tannins* states: "If, therefore, natural tannins are mixed with this product (Neradol D.) and the solution used for tanning purposes, the resultant leather will possess a dark color owing to the presence of solubilized phlobaphenes; if, on the other hand, a dark colored leather, which has been tanned with natural tannins, is washed over with a 5 deg. Be. solution of this synthetic tannin, or immersed for some time in the solution, the leather assumes a lighter color owing to the phlobaphenes being dissolved and removed from the leather by the synthetic tannin."

During recent years, combination tannages embracing the use of modern syntans have been greatly developed. It is now possible to manufacture excellent leather by combining syntans with vegetable extracts, basic chromium salts and formaldehyde. As syntans have a characteristic solubilizing effect on insoluble phlobaphenes present in natural (unsulphited) quebracho and chestnut, it is often a sound economy to make generous use of them when goods are to be finished either white or natural for shoe lining. The addition of synthetic tannin to vegetable tanning solutions

often improves the resistance of the finished leather to oxidation. When using certain cheap syntans there is, however, a strong possibility that the crust leather will be difficult to dye full, level colors. It will be remembered that the old Neradol leather suffered in this respect. If the syntan goods are to be dyed and finished in the ordinary way, then it is advisable to use a tan which offers no resistance to the penetration of either acid or basic dyes.

Syntans blend very well with most vegetable tanning materials, and as pointed out earlier, they have a natural solubilizing effect on certain difficulty soluble tannins. For this reason they can be used with natural quebracho to render it more soluble. Most synthetic tanning materials blend extremely well with sumac extract and the various tannates now available for producing white leathers are often mixtures of syntan and sumac extract. Syntans may be used either as a kind of pre-tannage, or added to the natural tan liquor towards the close of the tanning process. When using some syntans in a preliminary bath before the real tannage, it is recommended to take the goods straight from the drench or bate. Pickled goods should not be processed unless first de-pickled with borax or some other safe mild alkali. About 3–4 hours drumming with 3–5 per cent syntan (on pelt weight) is sufficient to fix the grain and ensure fullness and firmness of the finished leather. The writer has found that excellent results are obtained by treating crust leathers with syntan for re-tanning, and he considers this method preferable to the pre-treatment mentioned above. It should be pointed out that different syntans require different methods, and although some do not tan pickled goods very well, others react extremely well when drummed or worked with pickled skins.

Besides the ordinary straight syntans, there are now available a number of proprietary blends of syntan mixed with

vegetable tanning extracts, as well as blends containing specially selected synthetic materials and chromium salts. Leather tanned with these preparations is not only excellent in quality, but has a normal affinity for acid, basic and direct colors. One noticeable characteristic of these leathers is their level, clean color, and they take pastel shades particularly well.

For retanning imported vegetable tanned goods, such as East India tanned sheep and goat, Bagdad sheep, etc., synthetic tanning materials are of considerable value. Apart from their re-tanning action, which is, of course, the most important, they bleach the color and exert a beneficial cleansing action on the grain. Using Irgatan, 5 per cent on the shaved weight of crust leather, one hour's drumming at 40 deg. Centigrade, achieves the desired effect. Before tanning, it is always advisable to wash out the filth and excess tan, and if necessary, drum the goods in a weak solution of sulphuric acid to remove the iron stains. Some tanners prefer formic acid for this work.

The writer has found that the addition of a little sulphonated castor or neatsfoot oil has a most beneficial action on the penetration of some of the syntans now on the market. In the processing of natural white leathers, this oil might well be used in conjunction with 2–5 per cent colloidal clay. For natural shoe linings, the crust goods require washing with plenty of warm water 110 deg. F., then clearing with 1.5 per cent formic acid on the crust weight for 20 minutes. They should then be rinsed in warm water and drummed in 10 per cent of a suitable syntan for two hours, at the end of that time, 1.5 per cent sulphonated oil and 5 per cent clay should be added, and the goods worked for a further hour. This method can of course be adapted, but it will in its present form give good results.

The best modern syntans contain no free mineral acid,

the acidity being due to sulphonic and other harmless organic acid. This is important because it has been shown by more than one worker that sulphonic acids have no injurious effect on hide fibres when present at reasonable concentrations.

Sulphite-Cellulose Extracts

There has for some years now been a lot of controversy about the tanning abilities of waste liquors from paper mills.

Without wishing to enter the arena as a combatant, it is of interest to consider briefly the use of sulphite-cellulose extract in the processing of light leathers. One of the great advantages of all sulphite-cellulose extracts in the tannery is their solubilizing effect on ordinary quebracho. By careful blending, for instance, sulphite-cellulose extract, quebracho and chestnut, with, perhaps, a little myrobalans, it is possible to obtain almost any kind of leather at a reduced manufacturing cost.[1]

Apart from the solubilizing effect of sulphite-cellulose liquors, they help considerably to prevent the formation of sludge in tan liquors and increase the absorption of both tans and non-tans.

Failure to make good use of these materials is often due to neglect on the tanner's part to regulate the acidity of the liquors after the addition of the sulphite-cellulose solution. Proprietary extracts react in different ways towards the pH of the tan liquor, but where there is an increase, the addition of a little lactic acid is always helpful. Decrease in working acidity is always helpful. Decrease in working acidity is generally more noticeable in the case of soda base sulphite-cellulose extracts. When lime-base liquors are used there is often an increase of acidity and a lowering, therefore, of the

1 (Note: Mr. Smith is speaking of conditions in England, which may not always apply in America.—Ed.)

pH. When using sulphite-cellulose extracts, it is essential that the pH of the liquors should be accurately controlled by some simple means, such as the Comparator method, working always towards optimum figures.

In Europe, tanners seem to prefer the soda base sulphite-cellulose extracts, as these contain unimpaired all the valuable natural ingredients of pine wood, such as the tans, sugars, resins and other essential bodies. These bodies are often adversely affected during the production of lime-base liquors.

The writer has found that soda base extracts need more careful handling than the lime base liquors, but they can produce a better and firmer leather, and seem more suitable for the light leather industry.

Tanners using sulphite-cellulose preparations all stress the fact that they need most careful handling. Conditions of use must always be uniform, and strict chemical control is essential. There is still a lot of work to be done on these bodies.

Alum Tanning

The alums are double sulphates, the most important being aluminium potassium sulphate or potash alum. This is a colorless, crystalline, efflorescent salt made by mixing the two sulphates and allowing the compound to crystallize out of solution. Instead of using potash alum, some tanners make use of aluminium sulphate which is very economical in practice.

It is the aluminium sulphate in the complex potash salt that is really responsible for its "tawing" or tanning action. Procter points out that crystallized aluminium sulphate has a molecular weight of 666, and is of equal value of 906 of ammonia alum and 948 of potash alum. Aluminium sulphate itself converts hide into a hard and perfectly rigid kind of

leather which, however, is soon changed back into natural hide by washing in water. The addition of salt is necessary before a marketable leather can be produced.

Ed. Nihoul (*Collegium*, 1916, pp. 178–90), gives the following explanation of the action of salt: "Suppose in the case of normal tannage, in which sulphate of aluminium is mixed with sodium chloride. Between these two salts there is established as soon as they are placed in solution the following chemical equilibrium:

Since aluminium chloride has, like the sulphate, an acid reaction, hydrochloric acid is liberated in the solution, and since other things being equal, this acid is ionized to a greater extent than sulphuric acid (92 per cent against 62 per cent), it will be absorbed more rapidly and in greater quantity by the hide. The result is that the above reaction has a tendency to proceed from left to right, especially if the salt is present in sufficient quantity in proportion to the sulphate of aluminium.

The employment of this mixture has the following effects: First, to make the hide absorb a greater quantity of acid and consequently to increase the internal pressure. There are reasons for believing that this increase of presure increases the activity of chemical reactions if any are in progress; second, to liberate a greater quantity of aluminic hydrosol, and consequently to increase the quantity of basic salts found or else to give rise to salts of a more basic character, and at any rate to cause their more rapid formation; third, since there is more acid liberated, to form at first a greater quantity of acid salt which is apparently absorbed by the fibers, assuring a more perfect tannage; fourth, to leave in the tissues a notable quantity of aluminium chloride."

H. R. Procter gives a very lucid explanation of the action of salt in the alum tannage, thus:

"Alumina is a weak base, which readily gives up its acid in the pelt, becoming converted into a basic salt. The acid not only swells the pelt and renders it incapable of producing a soft leather, but the swollen pelt is less ready to absorb the alumina salt, and so remains under-tanned. The addition of salt prevents the swelling effect of the acid, and produces a partial pickling of the skin, which, in conjunction with the tanning effect of the basic alumina salt formed, yields a satisfactory leather, though one which is readily affected by moisture."

It is, of course, a well recognized fact in the trade that the aging process contributes a great deal towards the handle, durability and resistance of the leather to water. To prevent the ready hydrolysis of the alum salts is possible by impregnating the fibers of the skin with fatty matters, and successful alum tannages depend a great deal on the "fillers" used after or during tannage. These consist of oatmeal, flour, sulphonated oils, egg yolk, neatsfoot, olive and castor oils, also soaps. The use of soaps is, in the writer's opinion, important, because of the insoluble metallic soaps formed. These can protect and even waterproof the fibers and so protect the unstable basic salts. Although aluminium stearate is used to a large and increasing extent in the manufacture of artificial leather, waterproof cloth of all descriptions, etc., it does not find any appreciable use in the tannery, although it appears to be fairly well qualified for general waterproofing and protective purposes. The author has experimented with drumming straight alum leather in a colloidal solution of aluminium stearate with some success. This same method is used in the manufacture of waterproof cloth. The idea, of course, is for the hide fibers to absorb the colloid, which on wetting effectively seals the pores. Another method, which offers good promise, is to use aluminium stearate in the preparation of the fatty emulsion.

The use of egg-yolk makes tawing a somewhat expensive

process, but it is possible to fat-liquor the tawed goods with somewhat cheaper, but quite satisfactory substitutes. It should, however, be pointed out that there is nothing quite so good as the best egg-yolk, which contains all the ingredients necessary for the perfect lubrication of leather. Efficient egg-yolk substitutes are absolutely fast to acid and alum, and contain no fatty acid, which is often found in yolk. Many of these substitutes have a high lecithin content but unlike the natural yolk they are not coagulated at 55–60° C. which is rather important.

Colloidal clay and precipitated chalk are very useful additives to the fat-liquor. They should be as light as possible, and able to pass through a 150–200 mesh without leaving behind any harmful grit which is liable to scratch and damage the fine grain. For the best white kid, the use of pure titanium oxide is recommended. Besides improving the handle and color of the leather, the addition of a small percentage of titanium oxide to the fat-liquor gives the grain a much smoother and nicer feel and appearance.

Flour and oatmeal are other valuable ingredients of the fat-liquor and possess good feeding properties. Oatmeal is, if anything, preferable to flour. Some tanners like flour because it improves the color of the leather, but if good quality oatmeal is used there is no fear of stains or off-color.

Wetting agents of the sulphonated alcohol type are considered by many practical tanners to be quite unnecessary but in the writer's opinion they do help to increase the penetration of the fatty matters, and so promote fat-liquoring. Both natural and sulphonated oils should be used. Olive and neatsfoot oil are excellent, and they may be used in conjunction with sulphonated neatsfoot, castor, cod, or some of the heavy soluble mineral oils. To make the best possible use of oil mixtures it is always advisable to use a mechanical emulsifier specially suitable for the preparation of oil-in-water

emulsions. There are several really excellent machines on the market which can be recommended for this work. It is false economy, and often waste of valuable materials, to employ old fashioned and inadequate methods of emulsifying.

Some tanners overlook the great importance of the preliminary processes in the success of alum tanning. All goods to be alumed should be bran drenched in properly controlled bran drenches. The joint action of the lactic and other organic acids and the various fermentation gases help to render the skin in a condition for the proper absorption of alum liquor. Instead of drenching in the ordinary bran drench it is sometimes more convenient to drum the goods in a weak solution of lactic acid, which, except for the swelling action of fermentation gases, answers the same purpose.

After drenching, it is usual to drum the goods in a straight alum and salt liquor to set the grain, but occasionally this practice varies. In the production of alum tanned boot leather, F. T. Howard, (*Leather World*, Nov. 14, 1918) recommends wôrking the skins in a mixture of egg yolk, oil and flour.

"The flour, egg-yolk, and oil are mixed together carefully in warm water into a semi-liquid consistency, and in a small tub, which is placed in front of a tumbler. A skin is placed half inside the tumbler, the remaining portion hanging down to the tub in front to prevent the waste of any of the mixture. Skins are dipped into the mixture and carefully placed inside the tumbler until all the mixture is inside. If any skins remain they are thrown into the tumbler, the door secured as quickly as possible, and the machine started to revolve. In thirty minutes or so the mixture will have been absorbed, and without stopping the tumbler a tawing solution of alum and salt is poured in through the axle."

Howard recommends an alum liquor consisting of 6 per cent alum, with double the amount of salt, boiled together and used warm.

Excellent alum leather may be produced in many different ways, and there are really hundreds of good recipes. M. E. Amsterdamsky, *Cuir Trch.*, 1928, pp. 278–281, gives the following alternative formulae for alum glove leather.

7–9 lbs. flour.
3–3½ lbs. alum.
1–1½ lbs. salt.
6–7 egg yolks.
1–1½ liter water for each pound of the mixture.

This quantity of tawing is sufficient for 100 medium lamb-skins.

The writer recommends the following method of preparing alum leather, which is used very successfully in England for bag pipes.

The specially selected skins are well fleshed by machine, and then tumbled in running water (cold) for one hour. They are then bran drenched for 48 hours. Complete drenching is most important.

The alum solution is prepared by dissolving 100 lbs. alum, and 75 lbs. salt for every 100 lbs. pelt in warm water, 80 deg. F. When the alum and salt are both thoroughly dissolved and the solution cooled down to 60 deg. F. the goods are thrown in the paddle and the latter run for half an hour. Tannage is allowed to take place in the still paddle for two days. At the end of that time the skins are taken out of the liquor and hung up to dry in a warm stove. When perfectly dry and hard, they are weathered for several days, the longer the better, then tumbled in a mixture of oatmeal, clay and stock alum liquor to form a thin paste. About 8 parts of oatmeal to 1 of clay are recommended. The drumming is continued until the skins are thoroughly softened. They are then hung up again in a hot stove well weathered and stacked in a heap for about a week. At the end of that time they are drawn through warm water and bundled up to season before staking. After airing off in a hot stove, they are again

weathered, finally staked and buffed. This rather troublesome process certainly does produce a leather in every way suited for bag pipes. It will be noticed that no fat is used in the softening process.

With certain slight adjustments the above process works well for kid. Instead of using oatmeal and clay, a mixture consisting of egg yolks, neatsfoot oil, sulphonated castor oil and bentonite is recommended. As the skins are fairly light for gloving purposes, quite different from the heavy sheepskins used for bag pipes, it is usually only necessary to weather them once before staking.

B. Chazet and M. Zinder (*Vestnik*, 1930, p. 319), gives some very interesting particulars concerning tawing in Russia. After soaking, unhairing by painting and liming, hides are drenched and then drum tanned with alum and common salt. After tanning they are washed in an alkaline liquor and dried out. They are then well kneaded with natural fats.

Flemming, the well known American authority, states in his book, *Practical Tanning*, that soft, well-tanned leather results from tanning pickled skins with sulphate of alumina and salt to which egg-yolk and olive oil have been added. 100 lbs. acid-pickled skins can be tanned by using 3 lbs. of sulphate of alumina, 2 or 3 lbs. of salt, 5 lbs. flour, 2 lbs. of egg-yolk, and 1½ lbs. olive oil.

"The flour is made into a paste with a small quantity of cold water. The sulphate of alumina and salt are dissolved in a few gallons of water, and to this solution one to 4 ozs. of bicarbonate of soda is added, and the egg-yolk and olive oil are then thoroughly stirred in. Finally the flour paste is added and the skins are drummed with the mixture two or three hours, left in over night, drummed a while the next morning and then hung up to dry. When dry the leather should be kept in a clear dry room for some weeks before it is finished. It can then be finished white or colored any

shade. The skins are staked, buffed and drummed with 1 per cent egg-yolk and 5 per cent French chalk."

In the preparation of the fat-liquor it is most important that the various ingredients should be thoroughly mixed together to form a perfect emulsion. A mechanical emulsifier is really necessary, and the formation of the emulsion, also its stability, is greatly assisted if such substances a diglycol laurate or diglycol stearate are added to the mixture. There are on the market a number of these organic emulsifiers, many of which are well worth using where a good emulsion with penetrative powers is needed.

Alum tanning is not only by itself a valuable process for producing white leather, but it may be used in conjunction with other methods. Various alum and vegetable combinations have been described. Alum and oil tannage, also alum and chrome tannage, merit some attention. Excellent leather may be produced by stocking alumed leather with a mixture of degras and cod liver oil and treating in the same way as ordinary chamois leather. In this case the goods should be drenched in the usual way, then drummed in a mixture of alum and salt, ratio 2:2, dried out, weathered, softened by staking and then pushed into the faller stocks and well worked with a mixture consisting of 1 part of ordinary cod liver oil to ¼ part degras. When thoroughly saturated the goods should be hung up to oxidize in a warm stove, finally pressed to remove surplus oil and treated in the same way as ordinary chamois leather. Wonderfully soft and excellent leather may be produced in this way, but the process is rather expensive.

The writer has obtained very satisfactory results by drumming alumed leather in oxidized cod liver oil emulsion, and the process seems worth exploiting.

Splits were taken from the machines and after frizing to remove the layer of fat always present on sheepskins, they

are drummed in running water to remove as much lime as possible. After half an hour's working the goods were drummed in 1 per cent lactic acid until completely delimed. Drenching achieves exactly the same result and can be recommended, but it is not, of course, so quick.

Tawing was done with alum and salt solution; 75 lbs. alum, 45 lbs. salt per 100 lbs. pelt, and just sufficient water to process the goods at a temperature of 65 deg. F. After drumming in this liquor for 2 hours, the splits were allowed to remain in the alum liquor for 2 days. They were then drained for a day, lightly centrifuged to remove excess of liquor, and then dried out in a moderately warm stove. When hard and rigid they were weathered and seasoned down ready for rough staking just sufficient to open out the leather.

The oxidized cod liver oil was prepared by treating ordinary commercial cod liver oil with chromic acid. The amount of chromic acid used was 0.1 per cent of the oil by weight. Heating was done by steam and continued until no free chromic acid was found to be present in the oil. The dark mixture resulting from this treatment was emulsified with warm water with the aid of a proprietary emulsifier. The alumed goods were drummed in the emulsion for six hours, allowed to remain still in the liquor for the night and then drummed another six hours. Finally they were drained, lightly centrifuged and hung up to dry in a moderately warm stove, about 100 deg. F., and when thoroughly dry, washed up in warm water, 75 deg. F., containing a trace of free alkali. Finally they were centrifuged fairly thoroughly and dried out in an open shed. Softening was done by staking in the usual way and the goods finished off the same as ordinary chamois leather.

The leather produced is of excellent quality, somewhat tighter in texture than chamois but suitable for sports work. It can be dyed just as easily as chamois.

Alumed leather takes chrome very well, and the combination can be thoroughly recommended. Procter recommends commencing the tawing with an alum paste, and then adding a suitable basic chrome liquor when the paste has been completely absorbed. Flemming has found the following method very successful, one that is patented by George W. Alder, Philadelphia.

"The skins after drenching and washing, are drained and weighed. For every 100 lbs. of them a solution is prepared consisting of 3 lbs. of sulphate of alumina and 6 lbs. of salt in 3 gallons of water, boiled and allowed to cool. The skins are drummed in this solution twenty minutes. Then 10 lbs. of hyposulphite of soda are dissolved in 3 gallons of water and this liquor is poured into the drum and the drumming continued fifteen minutes. To finish the first part of the process, a third solution is prepared by dissolving in 3 gallons of water 2 lbs. of sulphate of alumina and 3 lbs. of salt. This solution is added to the contents of the drum and the drum run thirty minutes.

"The skins, now plump and full, are next rinsed off in clear water, drained several hours, and then given the chrome liquor which is used without the addition of water or acid. From 3 to 6 gallons of the concentrated chrome liquor are required for 100 lbs. of skins. The chrome liquor is prepared as follows: 5 to 6 lbs. of chrome alum are dissolved in 5 gallons of water without the aid of heat. To this solution are added from 2½ to 3 lbs. of sodium sulphate and from 12 ozs. to 1 lb. of potassium or sodium acetate, or its chemical equivalent. In a liquor thus prepared the skins are drummed one hour or until they are chrome tanned. They are then allowed to drain twenty-four hours, washed in the usual way, shaved and colored."

A simpler and very satisfactory method is as follows: Drum the prepared goods in a tawing mixture consisting of 5 per cent aluminium sulphate, 5 per cent salt per 100 lbs. pelt and just sufficient water to work the goods. Drum for two hours and then leave goods in the solution for a day, drum again for two hours, take out and drain. Lightly centrifuge to remove excess of liquor and then drum the skins

in a basic chrome liquor consisting of 4 gallons of chrome, 80 basicity and 135 grams of chrome per liter, per 100 lbs. of alumed goods. Drum for four hours, pile up on large trays over night, and next morning wash in running water for 1½ hours. Neutralize with borax, drain and treat in the usual way.

This method can, of course, be adapted in numerous ways, but in principle the adaptations are more or less the same.

Aldehyde Tanning

Certain aldehydes, the best known being formaldehyde, have a tanning action on hide substance. The mechanism of their action is still very uncertain and laboratory work has been rendered particularly difficult on account of the unreliability of hide powder as a protein for tests. Thomas, Kelly and Foster, (*Journal Amer. Leather Chemists Assoc.* 1926), comment upon the unsatisfactory nature of tests carried out with hide powder.

Aldehyde tannage has been explained as a purely chemical reaction between protein and formaldehyde, and alternatively as a physical adsorption of the aldehyde or its polymerization products by the proteins. Thomas, Kelly and Foster in their excellent review of literature state: "that the possibility of combination of formaldehyde with amino acids and proteins is not limited to a single 1:1 ratio, giving a methyleneamino linkage with amino nitrogen of the molecule, but that a triformal linkage with amino groups is also possible. Furthermore the work with condensed amino acids proves that fixation may also take place at the amino groups of the molecule. Evidently, therefore, a protein would be expected to combine chemically with relatively large amounts of formaldehyde."

Incidentally tannage increases with the concentration of

formaldehyde solution up to 2 per cent as pointed out by E. R. Theis and E. J. Schaffer (*J.A.L.C.A.*, 1936, 515).

The success of the aldehyde tannage depends to a large extent on the pH of the solution. According to Thomas, Kelly and Foster, the optimum range is between 7 and 9. Otto Gerngross and Reinhold Gorges (*Collegium*, 1926, 398–408), state that tanning at pH 3 was negligible but increased gradually to pH 6.3. They found a great increase in the tanning intensity above pH 6.3. By tanning sheep skins in concentrated salt solutions in which the swelling was repressed, it was found that no tanning occurred in acid solutions but in alkaline solutions good leather resulted.

According to E. R. Theis and E. J. Schaffer, (reference given above) little or no tannage takes place below pH 5, but at pH 5 and over the tanning is greatly expedited. They found that the addition of sodium acetate or formate expedited the tanning whilst sodium chloride had a slight retarding action. Sodium sulphate quickened up processing a little and the addition of this salt was found to reduce cracky grain in the finished leather.

There is little doubt that formaldehyde requires an alkaline solution for satisfactory tanning, and Grasses, (*Cuir*, 12., 230., 1923), states that the patents call for 1–1¼ per cent formalin with about 5 per cent sodium carbonate per weight of hide and equal volume of water. Tanning time is six to 48 hours according to size and thickness.

Thomas, Kelly, Foster recommend soaking the bated skins in a solution containing 10 to 50 grams of formalin per litre at pH 7 and to let them remain for about 24 hours. After washing with dilute sodium carbonate solution, fat-liquoring and if necessary, coloring, the goods are finished.

If properly dressed, aldehyde leather will keep indefinitely without deterioration. The author has some cuttings from leather tanned ten years ago which show not the slightest

sign of breakdown. As Wilson points out, if the pH is properly controlled throughout the tanning there is little fear of the leather becoming brittle and cracked as stated by Thuau and Meunier. Obviously the safest procedure is to maintain a pH between 7 and 8, but this is impossible in an ordinary tannery, and the practical man has to try and reconcile theoretical knowledge with works practice; not an easy job.

An excellent outline of the Payne and Pullman process is given by Louis A. Flemming in his book, *Practical Tanning*, —"400 parts of skins, after having been treated in the beamhouse in the ordinary way, are scudded and placed in a drum together with 500 parts of water at 38 deg. C. Then is added, while the drum is turning, the tanning liquor composed of 5¾ parts of formaldehyde (this is 14 parts of commercial 40 per cent formaldehyde) with 25 parts of calcined soda dissolved in about 50 parts of water. The drum is turned, and 5 parts of this liquor are added for a quarter of an hour. Light skins are tanned completely in three to six hours; heavy skins require from 12 to 48 hours. The temperature in the interior of the drum is then raised to 48 deg. C., and the skins are treated with a solution containing 16 parts of sulphate of ammonia in approximately 500 parts of water at 45 deg. to 50 deg. C. The skins are then taken out, nourished with 10 parts of soft soap and 10 parts of salt in about 350 parts water. They are tanned in this liquor for three to six hours, then washed, dried and finished."

A critical survey of this method will reveal many strange facts, and although it is possible to obtain reasonably good leather by using this formula, better leather can be assured by adopting less cumbersome recipes. The author has tanned excellent leather by taking the bated and scudded skins and drumming them in a 1 per cent solution of commercial formaldehyde for four hours, soaking for another four and then neutralizing with a little sodium carbonate followed by

fat-liquoring. There are no complications about this method, indeed it could hardly be reduced to any simpler form, but it is practical and economical.

For sheep linings the following method can be recommended. The linings are taken from the band knife machine and frized, either by hand, or run through the machine again to remove the fatty layer. Some tanners carry this operation out after a second liming, but it saves time and money to run the goods through the machine at this stage. The second liming is extremely important and the extent of the operation influences the feel and general characteristics of the finished goods. For very soft, stretchable leather intended for gloving, mellow liming is advisable for a period of not less than a week to 10 days. Sharp liming produces a firmer leather on the plump side. Straight lime liquors are the best, and the use of sodium sulphide or soda ash are not recommended as they appear to make the leather on the tender side. After reliming, the skins require washing and bating with an enzymic bate containing a fair proportion of ammonium salts. All traces of lime must be removed during the bating, and it is sometimes advisable to carry out a preliminary deliming with ammonium chloride. After scudding to remove as much filth and saponified grease as possible, the goods are ready for tanning.

It is a good plan to test the cut surface of the skins with a drop of phenolphthalein; a pink coloration should be given.

For 100 lbs. of stock, 1½ per cent formaldehyde and enough water at 90 deg. F. to cover the goods comfortably. A drum is recommended for the job as processing is not regular. If small lambs are being processed, three hours running will be sufficient, otherwise five hours is necessary for thorough penetration.

After horsing up for a couple of hours, the goods can be lightly hydro-extracted and then neutralized either with so-

dium carbonate or borax, both are very satisfactory. About ½ to ¾ per cent is sufficient. Some tanners use a mixture of equal parts of sodium carbonate and ammonium sulphate.

On the completion of the neutralization process it is a good plan to hydro-extract lightly so as to remove all surplus liquor. This should always be followed by a thorough washing in warm water, 90 deg. F. A drum provided with a lattice door is recommended for washing.

Horsing up and hydro-extracting should follow and then the goods can be fat-liquored. The composition of the fat-liquor must be carefully considered, and the author does not believe that a simple soap solution is nearly sufficient. Egg yolk is, of course, one of the finest ingredients of any fat-liquor, but care must be taken to see that its yellow color does not spoil the snowy whiteness of the aldehyde tannage. If plenty of kaolin is incorporated this tendency to yellow may be overcome. For ten dozen lambskins the following recipe is recommended:

10 lbs. flour
10 lbs. kaolin
10 lbs. best cured soap
20 egg yolks

The flour and clay should be made into a paste with cold water, then the soap dissolved in boiling water and when just tepid added to the first mixture. After thorough mixing and when the liquor has a temperature of 100° F. the egg yolks should be added and the solution thoroughly emulsified. A hot drum must be used for the processing, and the amount of liquor should be just sufficient to work the goods nicely. Two hours slow drumming is necessary for thorough feeding. Drying in a cool shed is advised.

Instead of cured soap, a good sulphonated oil can be used, preferably a fairly heavy one, such as sulphonated codliver or sperm oil. An alternative method is to use one-third

weight of soap together with one third the total weight of sulphonated oil.

Eitner recommends the use of neatsfoot oil and moellon. The addition of the latter is particularly useful if a yellow tint is to be given to the leather. The author has found that the two oils are best emulsified by the addition of a little triethanolamine soap, preferably the oleate.

There is no hard and fast rule in regard to formaldehyde tannage and it is possible to take all kinds of liberties with the original recipes. One of the most interesting of recent methods is described by Bocciardo and Genova who recommend a mixture of formalin and sodium silicate. The goods are pre-tanned with formaldehyde in the usual way, pH between 7.0 and 9.8, which can be adjusted by the careful addition of alkali such as sodium carbonate or borax, or sodium carbonate and ammonium sulphate. After washing, retannage needs to be carried out with an acidified solution of sodium silicate. The upper leather produced by this method is said to be very suitable for boot manufacture, being permeable and allowing the evaporation of perspiration. The snowwhite color makes the leather very suitable for summer sports goods. After treatment with sodium sulphate is also possible.

Little is known about the wearing properties of such a combination tanned leather. According to U. J. Thuau, *Evolution of Different Methods of Tanning*, (*Cuir techn.*, 9, 10, 80, 102, 1921), states that silica leather deteriorates on keeping and after a few months the fibres lose all their strength and the leather tears easily.

So far little work has been done with chrome-silica mixtures, although it would appear that commercially useful leather might be possible. A suggestion by the author is that the properly prepared goods should be treated with a ½ per cent solution of formalin, neutralized and thoroughly

washed. After a light hydro-extracting until just nice and moist, the goods might be drummed in an ordinary basic chrome solution for half the prescribed time, washed, neutralized and followed immediately by a further drumming in a 2 per cent solution pH 5, of sodium silicate, neutralized and washed again.

The author has tried out a method of pre-tanning with formalin ¾ per cent solution of pH 8 followed by neutralization with equal parts of sodium sulphate and ammonium sulphate, and then after washing in warm water to remove all traces of free alkali followed by hydro-extracting, the goods were stocked in the same way as chamois leather. The finished leather was of excellent quality and exceptionally strong and soft. Only a comparatively short processing in the faller stocks was found necessary to secure good commercial leather. Experiments with warm emulsions of moellon and soap seem to indicate that promising results may be expected by stocking aldehyde leather in heavy emulsions of this type.

Combinations of aldehyde and vegetable tannages do not appear very satisfactory, but good leather may be produced by combinations of aldehyde and a neutral synthetic tannin.

Oil Tanning

The idea of impregnating skins with animal fats and various fish oils and then allowing these to oxidize within the fibres is one of the oldest methods of converting putrescible skins into soft and naturally very resistant leather. In its simplest form the method is still practised by uncivilized tribes in various parts of the world today. Discussing oil tannage Procter says that "it consists merely in oiling or greasing the wet skins, and kneading and stretching it as it slowly loses moisture and absorbs fat. Under these condi-

tions the fibres become coated with a greasy layer, which prevents their adherence after they are once separated by the mechanical treatment. At the same time some chemical change takes place in the fibre itself, which has a part in its conversion into leather varying in importance according to the method and fat employed."

Some of the finest furs are tanned in the manner so ably described by Procter. The writer understands that in the reservation in Canada, the Indians still prefer animal fats for tanning furs—sometimes the fats are mixed with brains and flour. The famous "Helvetia" leather is fat tanned and is probably one of the strongest and most durable leathers produced.

The mechanism of oil tanning or chamoising is still imperfectly understood and the conclusions of Chambard and Michallet cannot by any means be taken as final. These two workers favor the view that chamoising is really a chemical reaction between the skin substance of collagen and an oxidizable oil, oxygen and water. The result of this reaction being to form a new and highly complex protein unit or molecule. They agree that the real tanning agents are the fatty acids present in the oil. It will be remembered that J. T. Wood was able to prepare excellent leather by means of free fatty acids isolated from fish oils. Although the tannage may, in part, be chemical, there is no doubt that the mere mechanical action of the oily bodies or soaps play a most important part in the lubrication of the fibres and water resisting properties of the leather.

Commercial Chamois Leather

The procedure adopted for chamoising varies considerably and every tanner has his own pet method. The following account is, however, representative of orthodox English

practice and is capable of giving excellent gloving and wash leathers.

The sheepskin linings from the band-knife or reciprocating blade splitting machines are first sorted into various sizes and qualities. They are then re-limed for a day or so in a used, that is, mild lime liquor. The object of this is to swell the goods so that the fatty layer will cut cleanly during frizing. This is best carried out over the beam by skilled workers, but in certain tanneries the limings are re-split on Reeder machines. Frizing or re-splitting, whichever method is preferred, is important as the layers of fat on the skin prevent the penetration of fish oil and also cause trouble at the finishing end. Strangely enough Procter states that the removal of fat is unimportant.

After frizing the goods require further liming for ten days. The procedure recommended is to start processing in a mild liquor for a day or two, and then in a fresher lime for a couple of days and finishing up in a new sharp liquor. Paddle liming is more economical and just as satisfactory as when carried out in pits. Hydrated lime is preferable to slaked quicklime.

On the completion of the liming process the goods should be allowed to drain for six hours, then thrown into a drum and washed with plenty of running water for two hours, or until the surplus lime is completely removed. Following this the skins require de-liming. Drenching is frequently recommended but a more economical method is to use a solution of acetic and formic acid, 1% acetic, 1% formic and 1% sodium acetate on the limed weight. Deliming should be stopped whilst the goods are still faintly alkaline, never on the acid side. They should then be given a brief wash and then hydro-extracted ready for milling.

Some tanners omit the deliming altogether and carry straight on with milling as soon as the free lime has been

washed away. Quite good results are obtained by this method, but the writer prefers the extra process.

The limings are taken from the hydro and packed in faller stocks where they are hammered for an hour to make them nice and supple and also to remove a certain amount of moisture. At the end of that time the goods are taken out of the machines, shaken out and allowed to cool down. They are then packed in the stocks and worked with codliver oil —Newfoundland variety is generally preferred—for two hours, adding the oil a little at a time until the goods will not take any more. The machines are again emptied, skins shaken out, placed in heaps and left for four or five hours. They are then once more stocked in oil and the mechanical action continued for six hours. At the end of that time the stocks are emptied, goods well shaken and piled in heaps to heat up. The piles are watched and if there is any danger of the skins becoming too hot they are shaken and aired. Next day stocking continues with fresh oil and goes on until the linings have assumed a dark, oil saturated appearance. Stoving then takes place. The skins are hung up in a hot stove, 100 deg. F., sealed and left for eight hours or more. Pungent fumes or volatile bodies, principally acrylic aldehyde, are given off during the oxidation of the oil and before the stove can be entered the air needs purifying by means of a powerful exhaust fan.

Further stocking usually follows stoving, then the oxidation is completed by packing the leathers into large tubs and allowing them to heat. This procedure requires very careful watching as it is easy to burn the goods and so ruin them.

At the end of processing, which is somewhat lengthy and expensive for genuine codliver oil tanned leather, the goods are soaked for 15 minutes in hot water, 120 deg. F., then packed in clean canvas and pressed in hydraulic presses to remove the excess of oil. This is dark and viscous. It is

known commercially as degras, although some tanners call it sod oil. After pressing, the chamois leathers are washed in a weak alkaline solution to remove the excess of fatty matter still attached to the fibres. A 1½% to 2% washing soda solution, preferably one which has been in use sometime and not a fresh liquor, temperature 100 deg. F. will be found quite satisfactory and will remove sufficient free oil in half an hour or so. At the end of that time the goods are washed up in warm water for 10 minutes, then hydro-extracted and dried off in a cool shed.

Several important modifications of the above process are worthy of consideration by tanners. It is, for instance, possible to pre-tan the linings with formaldehyde so that less oil will be needed and the tannage time considerably reduced. Another method to increase the penetration of the oil and so quicken up chamoising is to add 1½% on the limed weight of a suitable petroleum sulphonate to the oil. This product acts as a valuable coupling agent between the fish oil and the moisture present in the fibres of the skin. It also causes the water to become thoroughly emulsified. Several other glyco products are also well worthy of trial by tanners anxious to improve processing.

It is claimed by some workers that the addition of sulphonated oil to the fish oil improves penetration to a marked degree. Flemming recommends the following method. "The skins prepared in the usual way are passed through a 25% Turkey-red oil solution, whereupon they are allowed to dry and then laid in a moderately warm room in a heap and covered up. They are then next hung up in the air and allowed to dry slowly, when they are again oiled in the same solution after they have been laid in lukewarm water to rid them of any adhering unchanged sulpholeate, are filled, again laid in a heap, again dried, and then treated with a solution of alkali. The dry leather is then stretched and rubbed to give

it the softness that was lost in drying, and then completely oil-tanned."

Although very interesting, this method of Flemming hardly seems economical these days of high labor charges when the minimum number of handlings is desired. A useful adaptation of the process is to drum the hydro-extracted de-limed goods in a 25% soultion of sulphonated oil containing 2% diglycol laurate for 1 hour, then after hydro-extracting and partial drying to stock in oil. The first liquor can, of course, be used repeatedly providing it is strengthened occasionally.

The author has obtained excellent leather by drumming the properly prepared linings in a warm emulsion made up of oxidized codliver oil prepared by heating 5% chromic acid with ordinary Newfoundland codliver oil in the presence of a suitable catalyst. The mixture should be heated by means of live steam for four hours, then cooled and thoroughly emulsified with one of the new emulsifying agents, such as diglycol laurate, in a mechanical centrifugal emulsifier. If the goods are stocked instead of drummed a slightly softer leather is made. The author has a pair of gloves made of this new chamois and they dry clean and wash remarkably well.

Catalysts for chamoising have been suggested from time to time, and no doubt some of them serve a very valuable purpose. According to Chambard and Michallet the resinates of cobalt, iron, lead and manganese are capable of accelerating tanning to a marked degree. The percentage of catalyst is given as 0.01, which is very economical. Zinc resinate does not appear to have any appreciable catalytic action alone, but may, with advantage be added to other metallic bodies.

Experiments with synthetic tannings indicate that it is possible and practical to treat sheepskin linings with suitable synthetic tans prior to oil stocking. This can be carried out

as follows: Goods after deliming are drummed in a 10% solution of suitable synthetic tannin for four hours, allowed to drain, hydro-extracted and then stocked in the usual way. The method can, of course, be adapted to produce various types of leather possessing different characteristics. Whilst in the main there is little justification for the use of syntans for ordinary wash leathers, in the production of certain types of sports leathers where a fairly tight and more solid leather is required, then it might be that this method would be an advantage.

Bleaching Chamois Leather

Chamois leather can be bleached in a number of widely different ways. An old and favorite practice of tanners in England consisted of hanging the chamois leather in hermetically sealed rooms containing iron bowls full of burning sulphur. This is rather a clumsy method, but it has the great advantage of being cheap, and simple. A more satisfactory method is to process the goods in a weak solution of sulphur dioxide, sulphurous acid. This can easily be prepared by passing sulphur dioxide gas from a cylinder into the water in a drum of paddle. Good results can also be obtained by means of the permanganate method.

Briefly this consists of working the goods in a weak solution of permanganate solution until they have assumed a brownish shade and then reducing them with an acidified solution of sodium bisulphite, 2½%. The addition of 1% sodium acetate is recommended as a safe buffer which also tends to keep the leather full and soft. After bleaching with any of the chemicals mentioned, it is advisable to neutralize with a mild alkali and to give a short bath of sulphonated codliver oil or other suitable nourishing agent.

Bleaching is still carried out in the open by exposing the

skins to the rays of the sun. This is all very well for countries where the sun can be trusted, but for England the method is obviously no use.

For a pure white chamois a certain amount of pigmentation is necessary and the most suitable is titantium oxide which should be used in conjunction with sulphonated cod-liver oil and an emulsifying agent, such as triethanolamine.

Iron Tannage

During the World War, when vegetable tanning materials were both scarce and expensive, German tanners experimented with various substitutes including iron tannages but without apparent success. The writer understands that iron tannage is still regarded somewhat hopefully in Germany but nowadays the tendency is to develop combination tannages, often embracing the use of aluminum sulphate, chromium salts and certain organic compounds.

The latest work now being undertaken in Germany by the I. G. Farbenind A. G. appears to be devoted to the investigation of solutions of ferric salts with polycarboxylic compounds containing at least one double linking in the molecule. G. W. Johnson, I. G. Farbenind. A. G. (B.P. 462,026, 26. 8. 35) specifies ferric compounds ($FeCl_3$, $Fe_2(SO_4)_3$) combined with soluble albuminous substances, e.g., scraps from limed hides and skins suitable for making glue, leather parings, casein, horn, etc., and their soluble degradation products and derivatives, and the latter hydrolyzed by means of non-oxidizing proteolytic agents or an acid agent.

In pursuing their policy of self sufficiency, it is, of course, only natural that the present leaders of German industry should favor processes which do not depend for their success on the use of imported raw materials.

Although there is a wealth of patent literature dealing

with iron tannage since those first experiments of Johnson who took out an English patent protecting a method of using ferrous sulphate and hydrochloric acid, the actual progress registered has been extremely small. A point frequently overlooked by investigators is that iron salts act as catalysts and so accelerate oxidation both of the actual hide proteins and also natural fats present in the leather. Procter probably reached the heart of the trouble when he suggested that the futility of most attempts to produce commercially good iron leather can be traced to the reversible reaction which takes place when a ferric salt is present in the leather. This oxidizes the hide protein and so becomes reduced to the ferrous state in which condition, aided by the inherent catalytic action of the mixed iron salts, it takes oxygen from the air and so reverts to the original ferric condition. The cycle is thus completed and the disintegration of the leather continues apace.

The theory that the disintegration of leather is due to the oxidizing action of the ferric salts has, however, been challenged by D. D. Jackson and T. P. Hou (Iron Tannage J. Amer. Leather Chem. Assoc., 16, 63, 139, *202*, *229*, 1921) who state that the principal cause of brittleness in iron tanned leathers is due to bad technique rather than any chemical action due to the ferric salts. The method of tanning advocated by these two workers entailed the use of a basic solution of ferric sulphate prepared in a complicated and rather hazardous way. In the writer's opinion their process is of very little interest to the practical tanner who is certainly not willing to make use of chlorine gas in the preparation of tan liquors.

It should be remembered that it is the ferric and not the ferrous salt that has tanning properties. Basic ferric solutions are more certain in their action and give better leather than the normal salts. A. W. Thomas and M. W. Kelly

(Fixation of Iron by Hide Substance, Ind. Eng. Chem. 20, 632, 1928), define the basicity of the ferric solution as the ratio of equivalents of hydroxide to the equivalents of ferric iron in the salt. They prepared their basic solutions by adding caustic soda solution very slowly to the stock ferric sulphate solution until the desired or optimum basicity was reached.

The effect of neutral salts on the efficiency of the tanning solution can be quite appreciable, but Thomas and Kelly do not favor the use of sodium chloride. They state that sodium sulphate in low concentrations favors tanning with normal ferric sulphate. Possibly this is due, as Wilson suggests, to the introduction of sulphate ions into the ferric-ferrous nucleus. The addition of sodium acetate is recommended by the author as it appears to exercise a valuable buffer action and certainly improves the handle of the finished leather.

Experiments with Iron Tannage

The writer has conducted a series of tests with various iron tannages and obtained interesting and permanent results. This is the first time he has published results. The leather has been kept under observation for seven years and yet no deterioration of any kind has taken place. Pickled calfskin was drummed in a 15 per cent solution of salt for 15 minutes, then drummed in a 20 per cent solution of ferrous sulphate and 2½ per cent solution of sodium acetate (mixed in equal proportions).

After one hour's drumming the skin was taken out of the iron liquor and drummed in a solution of 1 per cent sodium dichromate and 1 per cent sulphuric acid for an hour and a half. It was then horsed up for 4 hours, washed, neutralized and dried out in a shed. The leather was tan brown in color,

somewhat thin and undernourished, but soft and strong; moreover its strength has been maintained.

A strong and light yellow leather was obtained by tanning pickled skin in a mixture made up of 20 per cent ferrous sulphate, 2 per cent sodium dichromate and 4 per cent sulphuric acid together with 5 per cent sodium acetate for 5 hours, washing well in running water, neutralizing with sodium sesquicarbonate and drying out in a shed.

At the end of seven years it was noticed that the leather showed a tendency to crack round the edges, but otherwise it appeared quite strong and generally serviceable.

An exceedingly simple method worked out by the author consisted in processing pickled calfskin in an acidified solution of sodium nitrite for 12 hours and then drumming in a 10 per cent solution of ferrous sulphate containing 2½ per cent sodium acetate for 5 hours or until completely tanned. The leather was a pleasant orange color and both soft and strong. This leather shows not the slightest sign of deterioration and compares most favorably with chrome. The yellow color obtained by treatment with the nitrous acid is no doubt due to the formation of a simple diazo dyestuff and tests seem to show that it renders the leather in a condition well able to take up ordinary coal tar dyestuffs more evenly and insures better penetration.

Iron tannage should not be carried out in wooden drums and as glass vessels are not available in the large sizes suitable for the tannery, the writer recommends the use of metal drums coated with an acid resisting resin and baked so as to give a hard, durable finish.

IV

CHROME TANNING

Chrome Tanning

Chrome tanning is a process which has received the most assiduous attention of chemists for many years. Most of the contributions made by chemists to our knowledge of this complex process are purely theoretical and cannot so far be translated into practice in the tannery. Although the evidence in favor of the formation of a complex chromium protein groups as sponsored by Wilson seems to be growing, there are still plenty of loose threads which require sorting out and it would be foolish at this stage to adopt a dogmatic attitude.

Two important groups of chromium salts are used in the tannery; the chlorides and the sulphates, the latter being the most important and producing the best leather. The reason for this has been explained by Gustavson, Ibid., 19.446 (1924), as being due to the fact that the basic chromium sulphate nuclei have a more complex structure than the basic chromium chlorides. It is possible, however, to render the latter more complex by the introduction of sodium sulphate during the early stages of tanning. Wilson in his book, "The Chemistry of Leather Manufacture," discusses this method. He says: "The tanning is started with very basic chromium chloride. Because of the very small relative size of the chromium nuclei, they penetrate into the skin very readily.

After a time sodium sulphate is run into the liquor in the tanning drum. This starts the formation of very complex chromium nuclei of high tanning value but with the chromium already evenly distributed throughout the skin."

Both chromium sulphate and chloride are used for the one bath method which was commercialized by Martin Dennis in 1893. His tanning liquor was a basic chromium chloride made in rather a clumsy way by dissolving washed chromium hydrate in hydrochloric acid and then adding washing soda to give a basic solution suitable for tanning. The one bath method of tanning was preceded by the two bath which was suggested by several independent workers in the late nineties, but was really put on a practical basis by Augustus Schultz in 1884. He recommended processing the prepared pelts in a bath consisting of 5 per cent bichromate of potash and 2½ per cent concentrated hydrochloric acid until they were yellow and thoroughly saturated with chrome.

After draining, the goods were then reduced in a hypo bath made up of 10 per cent hypo and 5 per cent hydrochloric acid. In principle the original formula of Schultz is still in general use today. There is quite a considerable difference in the characteristics of leather tanned in one and two bath liquors. Procter ascribes this to the presence of free sulphur in the latter. Box and willow calf, also light hides, are always tanned in one bath liquors which produce a firm, solid and yet fully supple leather with a fine, smooth grain. Gloving leathers, clothing leathers and glace kid are nearly always tanned in two bath solutions and the leather is very soft and feels well fed or lubricated. It is now possible to modify chrome liquors so that any desired characteristic may be obtained, but tanners still keep to this general ruling.

One Bath Chrome Tanning With Chrome Alum

The chemicals most used in chrome tanning are: chrome alum, $Cr_2(SO_4)_3 \cdot K_2SO_4$, 24 H_2O, which is obtained in considerable quantities as a by-product from the oxidation of a wide range of organic substances by a mixture of potassium dichromate and sulphuric acid. The dyestuff industry produces a large proportion of chrome alum as a by-product in the manufacture of alizarine, aniline violet and other well known coloring matters. E. W. Merry in his excellent book, "The Chrome Tanning Process," says that "the alum generally used is a potash chrome alum and a molecular weight which is near enough to 1,000 for all practical purposes (998 to be correct). It contains 10.4 per cent chromium whereas sodium or potassium dichromate contains 3⅓ times as much. If dissolved in water in the cold it ionises into the following ions [$Cr(OH_2)_6$ and SO_4, K^1]. The chromium content of this solution can be determined from the specific gravity, a saturated solution of specific gravity 1.0885 at 15 deg. C. containing 18.3 per cent chrome alum."

According to Merry, "the pH of the freshly prepared cold solution is 2.8 and the violet color is due to the complexion [$Cr(OH_2)_6^{'''}$] but on standing it gradually becomes green and progressively more acid as hydrolysis and secondary changes (formation of 01 compounds) occur. The hydrolysis gives rise to basic chromium sulphate and free sulphuric acid."

Chemists have for years argued about the respective merits of chrome alum solutions prepared by dissolving this chemical in hot and cold water. Apparently some workers consider that chrome liquors prepared by the hot method are superior to those produced by the cold one and give better

leather. Stiasny is, however, of the opinion that the best method is a compromise and consists in using both types of solutions. He recommends processing the skins in the cold prepared liquor at the commencement of the tanning process and then completing the operation with a solution made by dissolving the crystals in hot water. Apart from all other factors, it is quicker and more economical to dissolve the chrome alum in hot water than in cold. Flemming says that the leather is exactly the same produced by both methods.

The best way of dissolving the alum is to place the crystals in a fine wire mesh cage, or even strong canvas bag and suspend it in a large tub or vat containing the required amount of hot water. As the water takes up more and more alum it requires agitating to obtain even distribution of the chrome. Lamb suggests dissolving the alum in a rotating drum, but with this method there is always a danger of crystals getting lodged in crevices and at the back of the shelves and so remaining undissolved. Besides, every tanner cannot always afford a drum for this purpose and it is inadvisable in a small works to have a drum, the wood of which is saturated with strong chrome liquor.

M. C. Lamb in his standard work on "The Manufacture of Chrome Leather" states that for each "1,000 lbs. pickled pelt to be tanned dissolve

150 lbs chrome alum in
50 gallons of water at a temperature of
about 85 to 95 deg. C.

When the whole of the chrome alum has gone into solution cautiously add a solution, prepared by dissolving 11 lbs. soda ash or 40 lbs. washing soda crystals in 25 gallons hot water. The sodium carbonate solution must be slowly added to the chrome alum solution. . . . When the whole of the sodium carbonate has been added the solution should be made up to a total volume of 100 gallons and thoroughly

stirred. When prepared, the solution can be kept for any length of time before use."

Procter recommends 10 lbs. chrome alum per 1,000 lbs. pelt, but more must be used for the first parcel. He says that the bath gets more acid by use, and therefore as a safeguard before re-use it is advisable to add more soda solution. Little if any salt is necessary.

Flemming in his "Practical Tanning" considers the following recipe a good one:

"Dissolve 10 lbs. of chrome alum in 8 gallons of water, add 3 lbs. soda in a little boiling water, and enough cold water to make the alkali solution up to one gallon. Add sufficient of the soda solution to the chrome alum liquor until a clear liquor results, and then add a small quantity of salt. Ten gallons of liquor of 10 lbs. chrome alum will tan 100 lbs. skin." Flemming states that the chrome leather becomes fuller and finer and more nearly the chrome alum solution approaches the point of precipitation. It is, however, the author's experience that if a liquor is used near the point of precipitation there is always the danger of the grain of the leather being rather tender.

Procter states that "the quantity of salt to be added to the chrome liquor depends on the qualities desired in the leather, and upon whether chloride or sulphate liquors are employed; salt in chloride liquors increasing the softness of the leather, but in excess tending to flatness, while in sulphate liquors it practically diminishes their basicity by converting the chromium sulphate into the equivalent chloride, which as Eitner points out, behaves as a less basic salt, and hence but little advantage is to be gained from its use."

Wilson has done a good deal of work on the effect of neutral salts on basic chromium sulphates and chlorides and his experiments, as well as those undertaken by Thomas and Foster, Ind. Eng. Chem., 14, 132 (1922), go to show that

the addition of salt has a definite retarding action on the penetration of chrome and that the curves representing its effect all have "points of minimum followed by an upward trend, which, in the case of sodium sulphate, is shown only where the chrome liquor is very concentrated."

The amount of salt necessary for any particular class of

TOGGLE DRYING WHITE BLEACHED CHROME SHEEP INTENDED FOR SPORT WEAR . . .

leather must be determined by the tanner himself and he must take into consideration the pickle and preliminary treatment given to the goods as this has a most important influence on the tannage.

Neutralization

The most used alkali for this purpose is borax which has a very mild action on the acid chromium protein complex, and little or no action on the highly basic and olated chromium compounds fixed on or to the skin fibres.

Edwin K. Theis in an article entitled "Studies In Chrome Tanning," Journ. Amer. Leather Chem. Assoc., June, 1937, reaches the following conclusions:

"1. That all of the neutralizing agents used remove the collagen bound acid and some of them change the acid bound in the chromium salts fixed in the leather.

"2. That borax, ammonium bicarbonate and sodium acetate used in reasonable amounts in no way harm leather during neutralization and are to be preferred to many others.

"3. That ammonium bicarbonate used at a concentration of 1 per cent penetrates to the center of the leather and causes complete removal of any free acid from the leather. This reagent is an excellent neutralizing agent for chrome tanned leather just prior to coloring and fat-liquoring.

"4. That sodium acetate is also a good neutralizing agent, penetrating well and giving complete removal of free mineral acid when used at about 2 per cent. It may well be said that some of the sulphate groups are replaced by the acetate group during neutralization. The use of sodium acetate as neutralizing agent improves the physical properties of the finished leather."

The percentage of alkali must, of course, depend on its relative neutralizing powers as what might be perfectly safe

for borax would be dangerous for soda ash. One to one and a half per cent of borax is recommended for general work, but the writer has found that as much as two and a half per cent of sodium acetate is required for chrome upper leather. For the latter purpose he considers that sodium acetate is in many ways preferable and the extra cost is well justified. The introduction of fairly complex organic groups into the chromium protein compound tends always to improve the handle and physical properties of the leather, and the use of very simple radicals tends to break down the chromium complex with harmful effects on the finished goods.

Importance of Adapting Liquors to Correct Basicity

The most suitable basicity for any successful tannage depends on several factors:

1. The kind of skins to be tanned must be first considered. A suitable basicity for calf intended for box or willow uppers may not be suitable for sheep to be finished for clothing.

2. Previous treatment of the skins also plays an important part on the choice of basicity. Where calf and sheep are pickled in the same liquor and for the same length of time, then the conditions pertaining to both are practically the same, but when the sheepskins are taken to the tannery straight from the drenches they carry with them much less acid than the pickled calf, and for this adjustment must be made.

3. The nature of the chrome tanning solution, that is whether sulphate or chloride and also the percentage of neutral salts are other vital factors for the tanner to consider, especially as they all influence the effect of the basic chrome solutions on the goods in question.

In general terms it may be said that the basicity should be

retained at an optimum figure ascertained by the tanner from practical trials. Once this figure has been decided upon it should be adhered to for all packs passing through the chrome tannery. If the basicity is too high there is present a grave danger of too rapid tannage, undue swelling, irregular penetration and damaged grain. The other extreme, that is when the basicity is too low, is responsible for poor, empty and unsaleable leather.

Processing Notes

Adjustment of the basicity to the desired level is the next step after the alum has been made up into solution. It is a fairly simple matter to calculate the amount of soda ash or washing soda crystals needed to reduce the viscosity from the normal to any desired figure. Usually the tanner uses basicities ranging from 96 to 80 according to the type of leather he wishes to produce. The alkali must be added very slowly otherwise there is danger of precipitation. During the addition of the alkali the chrome liquor should be kept well stirred, preferably by some simple mechanical stirring device.

The pickled skins should be drummed in a 5 per cent salt solution for fifteen minutes prior to tanning. This tends to remove creases, open out the skins and induce a slight swelling of the fibres which facilitates the penetration of the chrome. The goods should be thrown into the chrome liquor made up to the required concentration and containing 1 per cent sodium chloride and 1½ per cent sodium sulphate. Drumming should continue at a steady rate for intermittent periods throughout the day. The best arrangement is to drum for 3 hours and allow goods to remain still in the liquor for 2 hours. Addition of stock chrome liquor must be

made very gradually and great care taken to prevent choking the fibres. When the chrome has fully penetrated it is a good plan to lay the skins out on zinc covered trays for 24 hours to feed. This gives additional weight and some solidity to the leather and is particularly recommended for chrome calf and kips for uppers. After traying, the goods require a further drumming in concentrated liquor and then immersing in the liquor overnight. Washing with plenty of warm water in a drum provided with a lattice door should follow tanning and after that neutralization with borax or sodium acetate. The final washing needs to be very thorough and the best temperature for the water is 100 deg. F.

Tanning Calf for Willow

This method is a very successful English one and produces an exceptionally fine leather.

For 800 lbs. pickled calfskin 50 gallons of water, 100 deg. F., and 50 lbs. salt are used and the goods drummed 30 minutes in a slow-drum. Allow to drain and then run on very slowly 24 gallons of chrome liquor containing 135 grms. per litre chrome and having a basicity of 80. Run for two hours and then tray up until next day.

Wash with plenty of cold water until washwater is crystal clear; this usually takes 1½ hours. Add 36 lbs. borax and run for 45 minutes. Wash a further hour, drain and then run on re-tan liquor through a large funnel. This liquor consists of the solution left over from the first stage of tanning together with 4 gallons of stock chrome. Run two hours and repeat the above operations of traying and retanning. Final washing should take 1¾ hours. The neutralization needs 26 lbs. borax and must be continued until the goods are only faintly acid as tested by litmus. They then require a final washing for one hour in water at 100 deg. F.

Commercial Chrome Extracts

In England the majority of these are chromium sulphates containing from 15 to 27 per cent Cr_2O_3 and 28 to 40 per cent basicity. Edwin R. Theis, E. J. Serfass and C. L. Weidner, "Properties of Chrome Tanning Extracts," Journal of the American Leather Chemists Assoc., April, 1937, state that "in the main these commercial extracts consist of 33 per cent basic chromium sulphate and sodium sulphate in equivalent molar quantities." In the use of these extracts they recommend that once the liquor is diluted it should be used before the complex chromium radicals break down into simpler ones. The tanning solution should be used when cold.

As a result of general practice in this country it has been found that it is more economical to use commercial extracts than chrome alum or a home made liquor from reduced bichromate. Chemical manufacturers are able to guarantee batches and also to reduce or higher the basicity to any desired level. In a large tannery where semi-chrome work is done it may be an advantage to use two or more different kinds of extracts, and some tanners find that chromium sulphate is not so suitable as basic chromium chloride for semi-chrome sheepskins intended for gloving and clothing.

Two-Bath Chrome Tanning

It is not intended to go into the history of the two-bath process of chrome tanning. The facts relating to its development are already well known, and in any case they are readily available in all good textbooks, probably the best account is to be found in H. R. Procter's book, "The Principles of Leather Manufacture." Since those early days of

Augustus Schultz, who adopted the process in 1884, there have been very few important alterations either in the actual recipe or the method of tanning. Considerable progress has, however, been made in the elucidation of the oxidation and the reduction processes.

The two-bath method of chrome tanning is one most used for glace kid, as it produces a soft leather with an exceptionally smooth, fine grain, well able to take a high glaze. It is also used in the manufacture of the best quality clothing leathers, which are superior to those given by a semi-chrome tannage.

In principle, the two-bath process is apparently quite simple, as it consists in the reduction of the chromic acid which, in the first bath, is used to impregnate the fibers. Thus, the color changes from a vivid chrome yellow to the characteristic duck egg green, really a bluish shade, in the hypo. The reduction of the chromic acid saturating the fibers is not as straight-forward as the reduction of a plain solution of chromic acid; the protein groups play an important part in influencing the reaction. According to Innes, who has done a considerable amount of work on various phases of chrome tanning, a certain amount of leathering takes place in the "yellow," due to the fixation of chrome on the collagen fibers. The effect of the fixed chrome in the "yellow" is an important but practically unknown factor, but it probably plays a part in bringing about that difference which every tanner can at once recognize between one and two-bath leathers. The main difference is generally attributed to the presence of sulphur in the second or hypo bath, but it is now realized that other influences are at work.

Slight variations in the method of tanning, or the proportions of chemicals used, reflect quite considerably on the tannage. Merry points out that "the addition of chromic acid to skins swollen with hydrochloric acid leads to a displacement

of the latter by the former with a disappearance of the acid swelling." The addition of neutral salt to the bath tends to decrease the amount of chrome fixed by the fibers. Successful tannage is really a matter of balancing these influences so that optimum conditions are maintained. From experimental evidence, it seems unecessary to add any salt to the chromic acid bath, as salt is produced by the action of hydrochloric acid on the dichromate, 3 lbs. of acid producing 1½ lbs. of common salt. In works practice, however, salt is always added as a safeguard to prevent excessive acid swelling.

As regards the time taken for "yellowing," there is a good deal of difference of opinion. Merry, in his book on "The Chrome Tanning Process," says "The goods absorb their full amount of chromic acid during four hours' drumming. To insure even absorption, drumming should be continued until at least two hours have elapsed from the commencement of the drumming. The drum may then stand overnight and be run for the remaining two hours next morning. Goods should remain at least four hours in the liquor, and even then the chromic acid solution may still continue to penetrate the fibrils of the skin more thoroughly."

To the present writer, this minimum time appears to be rather high and contrary to general experience, as excellent leather can be produced by only two hours' drumming in the "yellow." Merry is somewhat doubtful about the benefit of horsing up the goods out of the chromic acid, but most tanners consider this rather important, as it helps to improve the penetration, and fixation of the chrome is essential if the goods are to be struck out. A mistake often made is to pile the goods too high; this means that too much liquor is squeezed out of the bottom skins and not enough out of the top. The number of skins per horse should be fairly uniform and kept as low as possible; the load being distributed over as many horses as are available. Procter states that

goods in the "yellow" should always be protected from the action of the light, which reduces the chrome at the expense of the protein matter, and so causes damage by making the subsequent reduction irregular and patchy.

In the production of glace kid, there is no doubt that striking out in the yellow is a great advantage, as it keeps the grain smooth, and so improves the appearance of the finished leather. Another practical advantage obtained by striking out is that less acid is needed in the hypo bath and reduction takes place quicker. Too much pressure should not, however, be put on the "yellows," otherwise the tanned skins may be thin and poor, and there is even danger of splitting the grain. Sufficient pressure should be put on the rollers to remove creases.

Work in the yellow must be carried out with the greatest care and attention paid to detail. Variation in the amounts of salt, acid and chrome is liable to cause noticeable differences in the quality of the leather and it is, therefore, very important that strict uniformity of processing should be maintained by the tanner.

This is a typical English recipe for chrome sheep. For 800 lbs. pickled sheepskins, the following quantities are used:

Temperature, 110 deg. F.

Water, 50 gallons.

Salt, 50 lbs.

Hydrochloric acid, 1 gallon.

The goods should be drummed in this liquor for 30 minutes. At the end of that time, 58 lbs. of bichromate of soda dissolved in a small quantity of warm water, is added, together with 2¼ gallons of hydrochloric acid, and the temperature lowered to 94 deg. F.

When yellow and thoroughly impregnated with chrome, which usually takes about two hours, the goods are horsed up for three hours, so as to fix the chrome. They are then

thrown into a paddle wheel containing 110 lbs. of hypo and 1 gallon of hydrochloric acid. After the wheel has been running 15 minutes, 4 gallons of hydrochloric acid diluted with 5 buckets of water, is run on slowly. At the end of one hour, 50 lbs. hypo and 2 gallons hydrochloric acid, diluted with 5 buckets of cold water, are added, and at the end of a further hour, 20 lbs. hypo and ½ gallon acid, suitably diluted, added and allowed to work for two hours, then the goods drained and washed in cold water for 3½ hours (running water). They are always drummed in warm water, 100 deg. F., for 20 minutes before dyeing next morning.

Eitner gives the following method of two-bath tanning:

Per 100 lbs. pelt:

10 lbs. salt.
 1 lb. sulphuric acid.
10 gallons water.

To this pickle is added (after one or two hours' running) a solution of 3 lbs. bichromate, dissolved in a small quantity of water. Drumming is continued for two hours, or until evenly chromed. A solution of 15 lbs. hypo in 10 gallons of water is now added to the drum and 5 lbs. dissolved hydrochloric acid, gradually run in, in small portions. Eitner states that there is really no need to neutralize the leather, but it must be thoroughly washed in running cold water. If goods are to be fat-liquored, then neutralization is advised. Fat-liquoring should be carried out with olive oil and olive oil soap emulsions.

Another tried and successful recipe for chrome sheep makes use of the following formula:

36 lbs. salt.
33 lbs. sodium dichromate.
36 gallons water.
2½ gallons hydrochloric acid.
68 lbs. sodium thiosulphate.

5 gallons hydrochloric acid.

This is sufficient to tan 600 lbs. pickled pelt.

For chrome goatskins for glace, the formula should not differ very radically from that recommended for chrome sheep. Flemming gives the following recipe:

"For each 100 lbs. of pickled skins to be tanned, use bichromate of soda, 6 lbs. muriatic acid, 3 lbs. salt, 15 gallons of water. The liquor is prepared by adding the salt to the water, next the bichromate of soda, dissolved in hot water, and the acid is then slowly stirred in. A drum is used and, the skins having been thrown in, it is set in motion. The prepared liquor is poured into the drum through the hollow axle and the skins are turned for from one to two hours. They are then taken out of the drum and placed smoothly over horses to allow for draining and for the chrome to become fixed in the fibers. The process is completed the next morning. The skins are dipped, one at a time, into a 10 per cent solution of bisulphite of soda, and then thrown into a drum.

"The second bath consists of hyposulphite of soda, 12 lbs.; muriatic acid, 6 lbs.; salt, 3 lbs.; water, 15 gallons. The hypo dissolved in boiling water is added to the water in a tub. The salt and acid are then added, and the skins are drummed in the liquor for 1½ hours, or until they have assumed a light blue color throughout. This completes the tanning. The leather is again placed over horses to press and drain from 12 to 24 hours before it is washed and neutralized."

The author considers that a basic formula of the following type is preferable for glace kid:

Per 100 lbs. pickled skins:

5 lbs. hydrochloric acid.

7 lbs. bichromate of soda.

1½ lbs. sodium acetate.

15 gallons water.

The second, or reduction bath:

6 lbs. hydrochloric acid.

12 lbs. hyposulphite of soda.

15 gallons water.

The skins should be horsed up for 12 hours after chroming and then struck out, horsed up for a further two hours and then reduced. It is preferable to give the skins a brief run in the hypo before adding the diluted acid. Chroming should be carried out in a drum and reduction in a paddle. There is no need to neutralize the goods after reduction, provided they are given a thorough washing for three to four hours in running water, cold, and finishing off in 100 deg. F. for three-quarters of an hour. Some tanners find that neutralization, even with the weakest alkalies, has a harsh effect on the grain, and is therefore best omitted.

Treating Chrome Leather With Soluble Resins

H. R. Procter suggested some years ago that certain chemicals appear to have the property of rendering the fibres of chrome tanned leather supple and lubricated without the use of any oil or soap. His actual words in his book, "Principles of Leather Manufacture," are as follows: "The addition of, say, three parts of sugar, or still better, of glucose, to ten parts of the chrome-alum in making up the basic liquor, a much fuller and plumper leather is produced which dries perfectly soft, even without staking or fat liquoring, and it is probable that many other organic compounds may be found which produce similar effects." The author has found that many of the soluble resins act in exactly the same way as stated by Procter, and in addition they endow the leather with certain water resistant properties, which for uppers and clothing are particularly desirable and valuable.

In the textile industry, soluble resin formulas are now in extensive use for producing non-crush or non-creasing fabrics and also for "crinkling" rayon. Messrs. Tootal, Broadhurst and Lee brought out a patent about six years ago to protect a method of imparting non-creasing properties to textile fabrics by impregnating them with a water soluble solution of phenol formaldehyde and urea formaldehyde resins. So-called non-creasable ties and dress materials produced by this process are now widely sold. Referring briefly to methods of making various fibres permanently crinkled, A. B. Hall, writing in the "Textile Colorist," April, 1937, says that the new method consists essentially of impregnating the fibres, while in the form of yarn or other suitable form, with a synthetic resin in soluble form then crinkling them and at the same time or shortly afterwards hardening the resin to an insoluble form which simultaneously fixes the fibres in their crinkled condition.

A solution for treating viscose rayon, a suitable preparation can be made by mixing 50 grams urea and 200 c.c. of 40 per cent formaldehyde solution and boiling for 3 minutes, then cooling. About 4 c.c. of a 33 per cent solution of tartaric acid are added and the mixture further boiled for 10 to 15 minutes, afterward diluting with one-half its volume of water.

A simple urea formaldehyde resin prepared by merely mixing 250 grams urea and 100 c.c. formaldehyde and allowing to stand for six hours will produce a liquid which has the property of enabling chrome leather to dry out reasonably soft and with a good handle. The method of application is very simple. About a 10 per cent solution is sufficient to achieve the desired results. Drying can be carried out at a fairly high temperature without the leather suffering in any way; in fact, the higher the temperature the more water

resistant and stronger the leather (within reason, of course).

By further adaptation of the resin solution better results may be obtained. Thus if a mixture consisting of 250 grams urea, 75 c.c. formaldehyde and 20 c.c. furfural are boiled for 5 minutes and then diluted to make a 10 per cent solution, this will materially improve all grades of chrome and semi-chrome leather and will, in fact, enable full chrome to be dried out in a very hot stove without undue shrinkage or tinniness. The addition of sugar to the resin in the following proportions, 150 grams urea, 100 grams sugar, 100 c.c. formaldehyde is also successful and the solution is water clear and suitable for dressing white chrome.

The writer has prepared twenty variations of resin solutions and they all possess the property of rendering chrome leather able to dry out soft and well lubricated without the addition of any oil or fat. This soluble resin treatment enables the leather to stand up to the high temperature necessary for japanning with a urea resin for the preparation of a good class patent leather. The use of soluble resins in a bath prior to dyeing appears to have a slightly retardent effect on the affinity of the leather for the dye, but this is not very noticeable and may, in fact, be an advantage, as it tends to level the shades. There is no reason why the resin treatment should not be given after dyeing, although when this is carried out, certain precautions must be taken to see that the dyes are not affected by the mixed resins.

These resin solutions are cheap and easy to make and require no special plant. Although it takes somewhat longer to produce, there is no real reason why the solution should not be made simply by mixing the chemicals and leaving for five or six hours; boiling for three minutes is, of course, a good deal quicker and more certain, but the fumes given off may be rather troublesome. Boiling should not be continued

longer than five minutes, otherwise there is a danger of the resin suddenly solidifying and forming a completely insoluble resin similar to the range of Beetle and other commercial products. When once made and bottled or protected from further concentration by evaporation, these soluble resin solutions, which should always be diluted soon after making, will last indefinitely.

One rather interesting property possessed by this new leather is that it resists the penetration of water far better than the original untreated leather and it can, therefore, be washed repeatedly without losing that well nourished, full feel so necessary for all glove and clothing leather. It appears that the resin treated leather may find some use for treating hide and stout calf for the manufacture of uppers for army footwear to resist corrosive gases, such as mustard gas. This is only a suggestion but may lead to important developments.

Reviewing the experiments carried out by the writer, he considers that the addition of furfural is desirable as the furfural resin has more body than the simpler urea formaldehyde. One great disadvantage attached to the use of furfural is that if the resin mixture is prepared by boiling, then the fumes are very irritating and troublesome. Filling agents can be added to the resin mixture and the writer has used wax emulsions and methyl cellulose and obtained quite promising results. As a basis of further investigation there is no doubt that this resin treatment is interesting and may be important.

There is a possibility that these soluble resins may be of use for finishing both chrome and semi-chrome leathers. All that is necessary is to pass the resin treated leathers through hot rollers or press which converts the soluble resin into an insoluble form and also gives the grain a smooth, semi-lustrous finish.

Chrome Poisoning

This is one of the most troublesome of tannery hazards and one that is liable to affect a large proportion of workers. The experience of the writer is that susceptibility to chrome poisoning varies considerably and while some men are soon affected, others appear to be immune over a considerable period of time. Prosser in "The Dermatergoses or Occupational Affections of the Skin" denies this, and says:

"Some workers are said to show a greater constitutional susceptibility than others. Apart from textual variations in different people's skin, this statement is of doubtful correctness, so far as the skin trouble is concerned." A number of other well known workers oppose this view and quote many instances of hypersensitivity towards chromium compounds. Engelhardt and Mayer's Arch. f. Gewerbepath v. Gewerbehyg, 1931, ii. 140–168, state that 74% of sufferers from chrome eczema have a specific hypersensitiveness to the chemical.

It is a proven fact that the form the poisoning takes may vary very considerably according to the constitution of the individual. In volume I of "Occupation and Health," issued by I.L.O. Geneva, 1930: "According to the constitution of the individual one may find dermatitis of a vesicular or papular type with itching; it is difficult to cure. Sometimes the lesion appears as an eczema of a different kind with oedema and pains, often with an acute onset, especially when the workman has come in contact with hot solutions of bichromate. Among the sequelae of irritation of the skin, cases of septic granuloma have been reported."

Workers in the yellow should be healthy men with arms, hands and face free from all sores, abrasions or spots. Sufferers from chilblains are particularly prone to attack. Not

only are tannery laborers liable to be affected, but also men working striking out, or setting machines. The writer has found that a large proportion of these have one or two chrome sores usually on the knuckles and joints of the fingers which have to be bent over against the skins so as to pull them through the machine.

While it is an ideal arrangement to pick and choose workers for different operations, it is a fact, unfortunate or otherwise, that men are chosen quite haphazardly and when the chrome tannery is working to capacity, men from other departments are often drafted in regardless of whether they are suitable from a medical standpoint. This is unavoidable in a great majority of cases, but it must be realized that men accustomed to work with warm liquors, such as drenches and puers, often have swollen hands which, in the writer's opinion, are more liable to absorb chromium compounds than if they were accustomed to work with cold liquors.

As regards the actual sores formed by chromic acid solutions, the I.L.O. gives one of the most lucid accounts: "The ulceration of the skin commences in an insidious manner, without pain, with loss of substance and slight signs of infiltration, which, however, may increase rapidly and suddenly and cause a round hard ulcer sometimes under a scab; if the patient is not looked after the ulcer may become deeper and deeper and reach the bone of a joint. Cases are known where the joint and adjacent bone were laid bare. The lesion has no tendency to heal and requires prolonged treatment."

R. Prosser White says, "Chrome sores are usually situated at the roots of the nails, the creases of the knuckles, and the hairy parts of the backs of the hands and forearms. The skin between the fingers shows large numbers of skin-colored, painless, sub-epidermic, pinhead elevations. The web between the thumb and first finger is particularly susceptible to ulceration, if any crack is present. Previous laceration of

the cuticle or the mouth of the follicles, however, always determines the site of the ulcer which may be found on the wrist or arm, the penis, or groin."

A keen and conscientious foreman can do a great deal to prevent, or at any rate minimize the effect of chrome sores, by regular examination of his men's hands. He should not only look out for sores, but also any cuts or abrasions which need attention. Men with broken skin should not be allowed to work on the yellows even though their hands be protected by means of rubber gloves.

Protective clothing is, of course, necessary but too much faith should not be placed in the protective power of waterproof aprons, clogs and rubber gloves. These are satisfactory so long as no chrome is allowed to leak through and then they usually act as irritant compresses and aggravate the trouble. When rubber gloves and aprons provided by tanners get worn out, the stores quite frequently show some reluctance to provide new ones on grounds of economy. There is a kind of unwritten law in some works that gloves and aprons should last a given length of time, say three or six months, and if they don't, then workers are put off with the plea that the stock is exhausted and that they will have to manage for a bit!

While admitting that some men are far more careless than others, it rests with the employer to protect the health of the worker as efficiently as possible. It is interesting to note the remarks of Prosser White regarding the efficacy of gloves: "India-rubber gloves are often of more theoretical than real service, even in trades where at first sight they may seem most desirable. There are drawbacks to their use. As a rule operatives dislike them, an opinion which always required examination. They may contain the irritant, tetramethylthiuram disulphide.

"The presence of a waterproof material next to the skin

encourages heavy sweating, especially when working in hot liquids; perspiration soddens and removes the horny layer and thus renders the skin tender, thin and vulnerable to any active chemical. Sores, cracks and partially healed wounds are made larger and reopened by the use of gloves. Offensive exudations and pus organisms from the skin are retained and these latter reinfect or inoculate excoriated parts of the skin. Before gloves are worn, they must be scrupulously dry, clean inside and free from chemical particles or solutions."

Special ointments and salves are recommended for chrome tannery workers and the majority of these require rubbing into the cleansed pores of the skin and then all surplus removed by wiping with a clean towel.

An ointment suggested by Collis and Hunt and published in "Occupation and Health," Volume I, "is composed of mineral vaseline (1,360 grammes), soft paraffin (170 grms.) and cyllin (85 grms.). Levi, of Milwaukee, recommends the addition to the mixture of soft paraffin (three parts), lanoline (one part), and while warm, ten to fifteen drops of 90% carbolic acid. After washing the arms and hands with warm water the ointment is applied to the skin while still wet. It is rubbed in for two or three minutes; then the skin is wiped with a towel till no longer greasy." It is also recommended to wash the hands after work with a solution of a salt of bismuth (carbonate) or of zinc or calcium, or even bisulphite of soda.

Wetting Back Crust Chrome Leather

Although it is usual to dye chrome leather straight away after striking out, it is sometimes convenient to take the goods into the crust so that they can be carefully sorted and, if necessary, kept in stock for several months. Tanners often

find this a great convenience, as sorting in the crust is likely to be far more accurate and reliable than any sorting carried out in the pickling shop before tanning. Then again it is sometimes a great convenience to hold up production from the tanned state if there is any uncertainty regarding the best selling and most fashionable shades for smart uppers between seasons.

In the ordinary way chrome leather, when once dried out, proves extremely difficult, if not impossible, to wet back and some means have to be found to facilitate the wetting back process. Thanks to the use of new chemical wetting back agents it is now possible to treat tanned goods prior to drying so that they can be wetted back both easily and economically.

So-called "wetting agents" number several hundreds and patents are being issued almost daily to cover the manufacture and application of new ones. The property which all these highly complex organic bodies possess is that of reducing the surface tension of liquids.

Soap is, perhaps, the best known wetting agent, then follow the sulphonated oils, such as Turkey Red, the sulphated fatty alcohols and esters also substituted sulphonated naphthalene compounds and literally scores of others. Many of these are detergents of high power, although detergent ability is no great advantage to the tanner for this particular process. What particularly interests him is the property which some of these compounds possess of lowering the tension at the solid-liquid interface or where the fibres meet the liquid, and so increase its penetration into the body of the leather.

The procedure recommended by the author in the case of chrome leather is to treat it prior to drying with a solution of any suitable wetting back agent, which enables the dried leather to soften quickly and thoroughly at any future time.

After tanning, neutralizing and washing, the goods should be horsed up and allowed to drain for 48 hours. They can then be drummed in the minimum quantity of wetting back agent for at least 30 minutes, horsed up and drained for 24 hours and then, if considered essential, lightly struck out and dried. When it is desired to wet back the crust goods they should be drummed in a warm and weak solution of the same agent.

A recent patent No. 465,058 taken out by Burchill, Piggott, White and the Imperial Chemical Industries states that chrome leather, previous to drying and for the purpose of rendering it easily susceptible to "wetting back" is treated with a substantially neutral polyhydroxy compound containing at least one ether group or a polyether compound which may or may not contain free hydroxyl groups. Suitable substances are condensation products of carbohydrates with ethylene oxide, polyethylene oxide itself, cerols, condensation products of substances containing hydroxy or amino groups with ethylene oxide, polyethenoxyurea and fatty derivatives of such bodies.

In two of the several examples given leather is treated with (1) a solution of cane sugar ethylene oxide condensation product prepared by condensing sugar with ethylene oxide in the presence of caustic soda under pressure; (2) a solution of polyethylene glycol prepared by condensing ethylene glycol with ethylene oxide in the presence of caustic soda under pressure.

There are advantages and disadvantages attached to the use of these new chemicals. First of all, the advantages. It is, as pointed out earlier, a convenience at times to take goods into crust and this may often save the tanner both money and time in the long run. The use of wetting agents renders this possible both easily and economically and in addition improves the penetration of dyes and fat liquors.

The disadvantages may be summarized as follows: In the first place their use brings in an additional process, which of course costs money. The chemicals, usually branded goods, are expensive, especially if used at all carelessly. They are also apt, if the proportions are excessive, to render the leather too soft and cloth-like which is usually considered a great disadvantage. As they improve the penetration of dye, their presence often necessitates the use of more dye to obtain the required shade. This may seem a trifle paradoxical but it must be remembered that when chrome goods are dyed in the ordinary course of things it is only the grain layer that is really colored. Directly the color sinks lower, then obviously more is needed.

Considering the pros and cons it may be said that wetting back agents are very valuable assistants to the tanner if carefully and economically used. The minimum amount, which varies from 2–5 per cent according to the chemical, is recommended, but enough must of course be given to enable the leather to wet back without showing any hard spots.

It is a far better practice to treat the goods both before and after dying with the wetting back agent, than to rely upon the single processing of the crust goods.

Semi-Chrome Tanning

The semi-chrome processing is particularly applicable to gloving and clothing leather, where the price would not justify use of full chrome. Before vegetable tanned goods are chromed, the excess of tannin materials needs to be washed out and it is usually found necessary to strip the leather with a weak alkaline solution such as 1½ per cent borax calculated on the wet leather weight.

The crust goods are first drummed in warm water 90° F. for 20 minutes or until thoroughly soft and workable. The

addition of a small quantity of wetting agent helps considerably to get the leather into a suitable working condition and also improves penetration of the chromium salts during the tannage. The best known wetting agents are the sulphonated higher alcohols, but other bodies are equally efficient, particularly the sulphonated aliphatic esters of which group Betasol OT is well known in the United States.

The type of tannage plays an important part in the preliminary soaking, as some tannin bodies are washed out more easily than others and, of course, some vegetable tanned skins have a very much greater affinity for chromium salts than others. Myrobalans is a good ingredient of any tannin formula and when used in conjunction with quebracho makes a very economical and suitable tannage. There is, however, an objection to the use of quebracho insofar as it tends to contract the grain and so gives rather a harsh tannage. For this reason it is advisable to use quebracho more towards the end than the beginning of the tannage, which is best carried out in paddles.

After washing for 20 minutes in running water the goods should be stripped for 30 minutes in a 1½ per cent borax and washed in running water a further 20 minutes. This stripping is important and unless properly carried out it will prove impossible to produce a really soft, well fed leather.

There are several different methods of tanning but in the writer's opinion the best one is carried out with a basic chromium sulphate with a basicity of between 80 and 90. It is difficult and, indeed, undesirable to lay down any hard and fast rules regarding the most suitable basicity figure, but generally speaking, 85 is a good workable average. About 5–6 per cent basic chromium salt on the wet weight of the leather is needed for a full tannage.

This should be dissolved in water equivalent to the weight of leather and added in three portions to the drum. Prior to

tanning, some tanners consider it advisable to drum the goods with their own weight of 3 per cent salt solution, but the writer considers that a 2 per cent solution of sodium acetate is preferable.

After chroming for 3½ hours, the time depending of course upon the extent of re-tanning desired, it is usual to add about ½ per cent washing soda dissolved in water and to continue drumming for one hour and a quarter.

It is an advantage to horse up the goods overnight so that the chrome can set or become firmly fixed to the fibers and this practice is generally adopted by tanners in England. Next morning the leather requires thorough washing in running water for half an hour followed by neutralizing in ½–¾ per cent borax and then finishing off by a further washing in running cold water for ten minutes. When allowed to drain, skins should be set and shaved when they are ready for dyeing.

In the case of alum leather the process is practically the same except that stripping is omitted and washing time reduced by half.

V

DYEING, FAT LIQUORING, DRYING

Dyeing

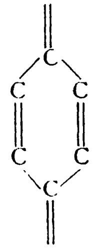
It is now generally known, even to that mythical creature "the man on the street," that coal tar is the starting-off point of the vastly important dyestuff industry. Although the number of dyes manufactured are legion, the raw materials and intermediates are comparatively few. Such well-known by-products of the gasworks as benzene, toluene, naphthalene, anthracene, phenol, cresols, etc., are the main sources of synthetic dyes.

To the practical dyer and non-chemical technologist it is puzzling to account for the wonderful tinctorial property of dyes, which, by the way, must not be confused with substances giving colored solutions not necessarily possessing any actual dyeing properties. In other words, colored solutions without any real affinity for fabric and which are easily removed by washing with soap and water, cannot be classed as dyes. Various theories have been evolved to explain why certain organic bodies can dye fabric, leather and other materials. One theory suggests that these bodies are dyestuffs because they contain certain characteristic groups known as chromophores (O. Witt.). Among these chromophores are ·N : N and NO_2. Although bodies containing these groups (known as chromogenes) are colored, they need other groups

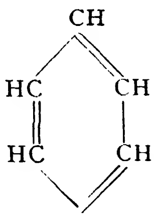
(so-called auxochromes) such as NH_2 (basic) or $SO_2{\cdot}OH$ and ·OH (acid) to convert them into dyes.

Thus nitro-benzene, a yellowish liquid chromogene, reacts with the NH_2 to form the dye Nitraniline.

Another theory is built on the supposition that the quinone group



which differs radically in molecular structure, or carbon valencies, from the benzene group, or radical,



forms an integral part of the dyestuff molecule.

Recent work on color constitution appears to indicate that an organic colored body is one possessing a certain degree of co-ordinative unsaturation, coupled with the property of producing ions.

Dyestuffs vary considerably in properties, such as brightness, fastness to light and rubbing, penetration and ability to produce level shades. Comparatively few dyes are pure and many of them are mixtures of two or more colors with certain innocuous materials such as sodium sulphate to increase the bulk. It is impossible to evaluate dyestuffs by

analysis and the only practical way is by means of trials with the materials it is intended to dye. Manufacturers try to make these trials as representative of tannery practice as possible. Apart from tests to determine the ability of the dye to color the vegetable or chrome leather, it is subjected to the most rigorous tests. One well-known manufacturing concern states that its "leather dyes are tested for fastness to aluminum sulphate, copper sulphate, ferrous sulphate, formaldehyde, formic acid, soda ash, sodium bichromate, stannous chloride and sodium hydrosulphite, all of which are used in the manufacture of leather. The dyes are tested for fastness to light and solubility in alcohol and water, influences which the dye will meet after the leather is in the hands of the user."

The Price Factor

Prices of dyes vary considerably and a great deal of confusion exists in the minds of tanners concerning the purchase of color. At the outset, it should be stated very emphatically that there is no such thing as a bargain in dyestuffs. Some very expensive colors have such a high tinctorial value and are so reliable and uniform in color that they are cheap in comparison with low-priced competitive dyes highly diluted, of the same shade. Good dyes are expensive, but it is courting trouble not to insist on the best.

Dyes Used in the Tannery

The two most used dyes in the leather trade are the acid and basic colors. The former are organic color acids which Parks and Beard (American Dyestuff Reporter, 17.6.35.) say "contain the color in the acid radical, dissociate in water

to give colored anions, form true aqueous solutions and are removed as the color acid by the fibre."

Basic dyes are "organic color bases which contain the color in the basic radical, dissociate in water to give colored cations, form true aqueous solutions, and are removed as the base by the fibre."

Procter, in his usually very lucid language, says that acid dyes "are the salts of organic color-acid with inorganic bases (generally sodium), and are usually readily soluble in water, but frequently do not fix themselves on the fibre till the color-acid is set free by the addition of some stronger acid to the bath, and in many cases the free color-acid is of different color to its salts. The 'basic' colors are salts of color-bases (organic bases of the nature of very complicated ammonia derivatives) with acids (mostly hydrochloric, sulphuric, or acetic)."

Basic dyes are generally distinguished from the acid dyes by the fact that they are precipitated by tannins and dye vegetable tanned leathers very rapidly.

In actual practice in the tannery acid dyes differ very considerably from the basic ones. They dissolve easier in water, produce more level results, especially on defective grains, and are faster to rubbing and slightly faster to light than basic dyes. The latter are also far more liable to bronze than the acid colors, and are in some cases, used specially to produce this effect. They are, moreover, particularly useful when it is desired to achieve great penetration of color or brilliant effects. It is not uncommon for dyers to top off acid dyed goods with basic colors. Apart from these two well-known groups of dyes, the direct cotton colors or chlorazol dyes are used for chrome and specialized dyes for brush dyeing or staining.

Many of the basic dyes are somewhat harsh and coarse colors; incidentally, some of them were responsible for John

Ruskin's classical remarks regarding synthetic dyes as compared with natural coloring matters. Fastness to light varies considerably, and on light shades fading is often very noticeable. Methylene blue is, perhaps, the fastest and most valuable of this group, Bismarck brown also being a very serviceable color. M. C. Lamb, who has done some of the most valuable work on the practical aspects of leather dyeing, found that a number of basic dyes are faster to light on leather than on textiles. No satisfactory explanation has so far been given to account for this extra fastness, but it is well-known to dyers in the trade.

Although fastness to light is, of course, important, the increasing use of pigment finishes, either water bound or in the form of cellulose lacquers, prevents to a great degree the penetration of chemically active rays. The fact that catechol tannins discolor badly on prolonged exposure to light, complicates the matter and may result in considerable patchiness. In the case of brown shades, which after all are the most popular, fading or tannin discoloration generally passes unnoticed.

Nomenclature of Dyestuffs

Dyestuffs are generally known by means of three identification marks which indicate the trade name, shade, and manufacturer. The letter immediately after the name of the dye gives the clue to the shade. Thus Y stands for yellow, B for blue and so on. The number immediately preceding this initial gives some idea of the degree of the shades. Thus some dyes are made in six or even more shades; methyl violet is a good example and may vary from a full purple to violet and red. Bismarck brown also varies considerably in shade and there are over a dozen adaptations.

When ordering a dye great care should always be taken

to give the fullest particulars regarding its manufacture and identification. Omission to give this essential data may lead to considerable confusion and possibly cause the wrong dye to be purchased or used.

Value of Recipes

The greatest value is set by some dyers on their recipes, many of which are handed down from father to son and only slightly adapted during a number of years.

Whilst some of these are extremely useful, others are definitely wasteful as well as being uncertain. The writer has known dyers to use as many as seven or eight dyes to obtain a certain color effect which could have been achieved by the use of two or three at the most. This attempt to make the job of dyeing more complicated can often be traced to fear —fear that someone else, who is probably just as capable and no doubt years younger, will step into the dyer's shoes. There is no need for secrecy or mumbo jumbo in dyeing leather and any tendency this way should be discouraged by the management. Most dyeing recipes could quite easily be standardized without any deterioration of results.

Storage and Weighing Out of Dyes

The dye store room should be large enough to provide accommodation for all the dyes necessary, and allow for easy and quick identification and handling. Too often the store room is not much larger than a cupboard and the foreman has to move several tins and barrels before he can find the color he wants. This entails serious waste of time and may entail some risk of weighing out the wrong color. The writer has known this to happen more than once because of

some keg or tin losing its label through being pushed in a corner or against a wall.

Accuracy in weighing out color is important, as a careless foreman, who is not particular to half an ounce either way, can soon waste a lot of expensive dye. It is recommended that two scales should be used, one for pounds and the other for ounces and parts of an ounce.

Disolving Dyestuffs

The main trouble in dissolving dyestuffs is encountered when hard water is used; hardness in water adversely affects solubility. It is always advisable either to use softened (but not alkaline) water or else boiled water. The water to which the dye is added should not, however, be boiled up with a live steam pipe, as some dyes such as Auramine, are broken down as the result. For this dye no temperature above 140° F. should be used.

In the case of acid and direct dyes the best practice seems to be mix with cold water to form a thin paste and then to add sufficient boiling water so that all the dye goes into solution. The concentrated color requires sieving before use to avoid all chance of undissolved particles being present in the liquor. These cause serious stains, especially with very light pastel shades.

Basic dyes should be made into a paste with a little acetic acid, 30% strength, and the boiling water added to this so as to make the concentrated liquor ready for use.

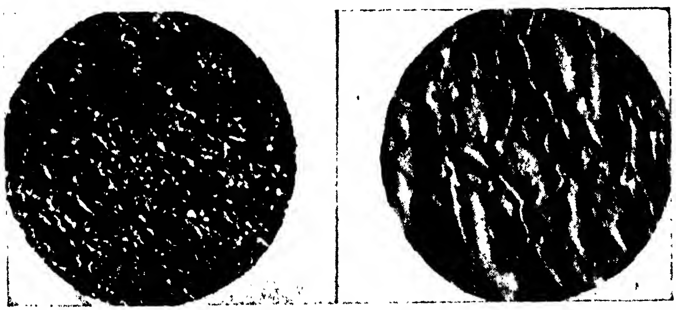
Acids for Use with Acid Dyes

Until a few years ago sulphuric acid was used for developing the color, about ¼–½ lb. D. O. V. to each pound of

color. Owing to the deteriorating effect of this acid on the leather fibres, most tanners now make use of the milder organic acids, formic and acetic. These are, however, considerably more expensive in use, as two to four times as much acid has to be used to obtain the same effect. The amount of acid varies slightly, according to the method of dyeing and the shade. In the case of drum dyeing, the volume of liquor being comparatively small, three-quarters the amount of acid used for paddle dyeing would suffice.

The acid, diluted with 5 to 10 times its volume of cold water, is usually added after twenty minutes processing with one-third of the weight of acid dye.

Formic acid is most used as a substitute for sulphuric, but acetic acid seems equally effective as shown by H. Salt, who found as the result of a long series of tests that "In no case was the color development better using sulphuric acid. In some cases it was not quite so good. Certainly the advantage



LEFT: PHOTOMICROGRAPH OF GRAIN OF SKIVER RENDERED BRITTLE AND BISCUIT-LIKE BY USING TOO MUCH MINERAL ACID IN DYE BATHS. RIGHT: GRAIN OF SKIVER SHOWING LESS INTENSIVE DAMAGE.

was on the side of acetic acid in considering level dyeings as a criterion of efficiency." M. C. Lamb, in his book on

"Leather Dressing," writes that "Lactic and acetic acid are of little value in this direction, the finished leather, when either of these acids has been made use of in dyeing with an acid color, is pale, lacking in brilliancy, and altogether unsatisfactory."

The writer's own view is that formic acid is preferable, but that for many dyes, acetic acid appears to give quite good results. To ensure this, it is necessary to use at least one-third as much acid by volume than formic.

Importance of Regulating the Quantity of Water

It has been pointed out on more than one occasion that the volume of water should be calculated as carefully as the acid and dye. Considerable variations in the amount of water used must influence the shade and, unless uniformity is ensured, a serious handicap is placed on the dyer who tries to obtain consistent results. D. McCandlish and H. T. recommend 500 per cent on the sammed weight. In actual practice the experienced dyer is careful to see that the same amount of water is run in the drum or paddle for consecutive batches of goods, but it is very rare indeed that it is even roughly measured.

As long as uniformity is aimed at, the actual volume does not matter so much. The writer knows of one dye house where the paddles are all marked at the proper level, so there should be no confusion regarding the volume of water for all dyeings. This is rare, as what usually happens is that a laborer is given the job of running in the water and if the volume "looks all right," then that is considered near enough by the foreman.

Methods of Dyeing

There are four methods in use today, although the first is only carried out for special classes of goods where an undyed flesh is required

1. Tray Dyeing
2. Paddle Dyeing
3. Drum Dyeing
4. Staining

Tray Dyeing

This was the standard method until the introduction of drums and paddles. For level dyeing and undyed fleshes there is no doubt that dipping is unequalled and in most tanneries occasional batches are still tray dyed. The method has many obvious drawbacks. First and foremost it is expensive and slow. Secondly, tray dyeing makes it difficult to obtain consecutive packs of exactly the same shade.

The trays are usually just simple wooden boxes about 10 inches to a foot deep and of sufficient size to allow for easy manipulation of the skins to be dyed. M. C. Lamb gives the proportions as 4 ft. 6 ins. long by about 3 ft. 6 ins. and 9 to 10 inches deep for sumach goats, roans and skivers; for calf skins and large skivers a tray 5 ft. 6 ins. long, 4 ft. wide and 12 ins. deep is specified.

The skins are dyed in pairs and the procedure is as follows: Crust goods are trimmed and, if necessary, shaved, then wet down thoroughly and often given a preliminary treatment with warm sumach liquor in a drum (10 lbs. good Sicilian sumach per 100 lbs. dry leather), followed by a light rinsing in warm water. The goods are then struck out by hand and skins of the same size properly paired and left

overnight so that they stick together and can be handled in pairs fairly easily.

The next day the tray is filled up to the proper level with warm water, 50 deg. C., and half the dye, together with all the acid, added to the liquor and stirred round thoroughly so as to ensure perfect and uniform solution. The goods are then placed in the liquor and as soon as the complete pack is in the tray, turning commences and the goods kept in constant motion. Actual method of turning varies and dyers usually work out their own special methods.

M. C. Lamb gives a very practical method: "The top pair of skins is lifted and turned over, and placed at the right hand end of the tray. The succeeding pair is then treated in the same manner and so on until a quarter of the pack or thereabouts is at the right-hand end. The pack at the left hand being thus lightened, the pair of skins at the bottom of it can be pulled out, turned over, and placed on the right-hand pack, and so on with all the other pairs at the left-hand end. Similarly working with the now full pack at the right-hand end, it is transferred to the left hand and the working from end to end in this way is kept up until the operator judges that all the pairs of skins in the pack are in equal condition as regards their dyeing." At the end of half an hour, the remainder of the dye is added.

Attempts have been made with varying success to mechanize tray dyeing or dipping, and some of these methods are highly ingenious and useful for special orders.

Paddle Dyeing

Whereas, with tray dyeing only the grain is fully colored, both flesh and grain are evenly colored when dyed in a paddle. Naturally, more dye and acid are used in the paddle than the tray, but paddle dyeing is quicker and more eco-

TESTING THE FASTNESS OF DYED GLOVING LEATHER TO WET RUBBING. IT IS VERY IMPORTANT THAT THIS TYPE OF LEATHER SHOULD BE ABSOLUTELY FAST. . . .

nomical for large and medium packs of goods. Movement through the liquor is sufficient to ensure level results, and there is no fear of damage to the goods through the action being too drastic.

All dye paddles should be provided with light wooden

covers so as to maintain the temperature at a constant figure throughout the operation. The dye and acid should be added to the water in the paddle by means of a trough which enables the color to be evenly and swiftly distributed throughout the liquor.

Only the best paddles—that is, those where the goods are kept in constant motion with no dead spots—should be employed for dyeing.

Drum Dyeing

Important advantages may be claimed for this method, especially for heavy goods. Penetration of color is better than with any other method; economy can be practiced in both the quantity of dye and acid used and the temperature can be kept at a constant and optimum figure without difficulty.

There are, however, two main drawbacks to drum dyeing: Firstly, the action is violent and often causes damage to the skins, contracting the grain and even causing tender goods to tear badly; secondly, as the door has to be removed every time the skins have to be inspected, a serious obstacle is placed in the way of proper supervision.

The best type of drum for dyeing has a door in the center which is light to handle and fits tightly in its seat. Feeding of dye, acid, etc., should be made through the hollow axle of the drum instead of through the door. Shelves are preferable to pegs and with them there is much less chance of damage to goods or the formation of troublesome knots.

Temperature Control

It is important that the dyer should be able to see at a glance the temperature of the dye liquor. There is no dif-

ficulty about fixing a thermometer so that it registers the correct heat of the paddle liquor, but in the case of the drum it is more difficult. By means of a little ingenuity it is, however, possible to fix the thermometer so that the bulb is immersed in the liquid when the drum is stationary.

There are several electrical devices now on the market which are not only very accurate, but seem in many ways very suitable for use in the dyehouse. The temperature of the dyestuff solution should be higher than 95° F., but must not exceed 140° F. A good average is 115° F.

Dyeing Chrome Tanned Leather

Chrome leather is usually dyed in the drum, as this method helps to insure better penetration and also enables fat-liquoring to be carried out at the conclusion of the dyeing operation. Acid, basic and direct cotton colors, are all used to achieve special results, and it is not uncommon to use two different dyes to obtain improved penetration; thus chrome goods are often bottomed with acid dyes and topped with basic colors; alternatively they are sometimes blacked with mordant and an iron salt and finished off with a good chrome black dye.

It is generally recognized that dyeing chrome leather is considerably more difficult than dyeing vegetable tanned skins, especially if it is necessary to obtain good penetration, as in the case of suedes. Mordanting with sumach, gambier, fustic and peachwood, is generally advisable to insure even coloring, but great care has to be taken to prevent this retannage process from altering the characteristics of the leather to any noticeable extent. Some of these mordants have a decided tendency to make the leather cloth-like, and gambier is one of the worst offenders.

Black and brown shades are in most demand, but for

glace kid it is now becoming the fashion to provide a very varied color rånge, including some of the most delicate pastel tints. When the latter are required, it is advisable to bleach the tanned goods so as to obtain a more uniform and lighter surface which will not be likely to influence the color. Bleaching may be carried out with permanganate of potash and sulphurous acid, or a suitable synthetic tannin, which will not be likely to obstruct the penetration of dye. Full information regarding bleaching of chrome leather will be given in a later section of this work.

The importance of complete neutralization and exhaustive washing cannot be too fully emphasized. It has been conclusively demonstrated in the laboratory that the success of the dyeing operation depends on several factors, one of which is the degree of neutrality of the leather when it enters the dye bath. One of the most recent reports on this phase of dyeing is by E. Belansky and Z. Kratky, Technicka Hlidka, Kozelnzska, 1937, 3, who found that, unless neutralization of the leather is scientifically controlled, it is possible to obtain wide differences in the pH of different parts of the surface of the skin. Their experiments showed that the pH is always inclined to be higher in the butt than in the neck or sides, i.e., butt 6.59, neck 6.32, side 6.25. The grain side has a lower pH than the flesh.

Further interesting facts contained in the account of the work of these chemists relate to the pH of dye solutions. Tests showed that aniline dyes have widely different pH values, direct and acid dyes having a pH between 5.0 and 9.0, and basic dyes from 2.0 to 3.0. In dyeing with direct dyes, they recommend that the pH should never be allowed to fall below 5.0, and not below 4.0 with basic dyes.

Although, as pointed out in the above paragraph, it is desirable to exercise the most careful control over the neu-

tralization, it is not usually possible in a busy tannery to make use of elaborate electrometric methods. The only practical way is to determine the best method for average packs of goods, to check this with all the resources of the laboratory and, when it is passed, to adopt it as an empirical method, subject to occasional checks. Provided goods and alkalies are carefully weighed, amounts calculated correctly and time unaltered, there is little chance of error creeping in, but it should be insisted that only a fully experienced and reliable foreman should be responsible for the process. As mentioned previously, washing is almost as important as neutralization, as, unless neutral salts are washed away completely, there is a likelihood of trouble arising through spue, and maybe uneven penetration of fat-liquor.

Some dyers favor fat-liquoring goods before dyeing and to facilitate penetration of dye they add a small quantity of ammonia to the dyestuff, usually about 1½–2 oz. This method, although capable of excellent results in skilled hands, further complicates the whole process of manufacture and may result in patchy dyeing, especially in the case of light colors. It is far preferable, in the writer's opinion, to carry out the fat-liquor at the completion of the dyeing process, using about one-half of the liquor which can, if necessary, be heated up with steam.

This is generally favored by English tanners and is, in fact, the method advocated by M. C. Lamb in his book dealing with "The Manufacture of Chrome Leather." He writes, "Run off two-thirds or three-quarters of the waste dye solution, blow a little live steam into the vessel whilst it is still rotating, in order to bring the temperature up to the required temperature, 120 to 130 deg. F., then add the fat-liquor emulsion which has been heated to a temperature of about 140 deg. F."

Dyeing Chrome Leather with Acid Dyes

For every 100 lbs. leather (shaved weight) run into the drum 13 gallons of water 125 deg. F. Half the sieved dye-stuff solution is then run through the hollow axle of the drum after five minutes of drumming the goods in plain warm water. At the end of five minutes' dyeing, the remainder of the color is added and drumming continued for ten minutes. The diluted formic acid is then poured in, two parts of concentrated acid to every four parts of dye, by weight. Drumming should continue for another ten or fifteen minutes. At the end of that time the goods can be examined, half to three-quarters of the exhausted dye liquor run off and the fat liquor emulsion added. If the latter is at a temperature of 140 deg. F., it will bring the remainder of the liquor up to a reasonable temperature.

Some dyers recommend rinsing the dyed goods before fat-liquoring, but the writer cannot see why this should be necessary, and, in any case, it is an expensive, extra process. If the above method is adopted, there is no reason why completely successful and uniform results should not be obtained.

The addition of sodium acetate, one part to every four parts of dye, helps materially to improve both weight and handle of light hides and calf for shoe uppers.

Combining Acid and Basic Dyes

This method is specially recommended for blacks; also for dyeing certain colors where the goods are known to be faulty. Double dyeing helps considerably to mask grain defects.

Carry out the acid dyeing in the manner described, using one-half to three-quarters of the normal amount of color.

At the end of the dyeing operation, add a suitable mordant dissolved in a small amount of water, say two gallons, and continue drumming for twenty minutes. Now add sufficient basic dye dissolved in acetic acid to obtain the desired shades; drum for twenty-five minutes; run off one-half the solution and fat-liquor in the usual way.

Instead of mordanting half way through the dyeing process, the mordanting may be carried out before dyeing with the acid colors. The writer prefers the above method, however, as it enables more even penetration of dye and is equally, if not more convenient.

The addition of a small amount of ammonia, about one-quarter per cent of the weight of acid dye, is advisable where the fullest penetration is necessary. In this case the ammonia should be added with the second portion of dye and extra acid must be used to neutralize the alkali, say 2½ parts of formic per four parts of dye.

Dyeing with Basic Dyes

In order to dye successfully with basic colors, it is necessary to mordant the leather with one or other of the better known tannins. Fustic, logwood extract and gambier are recommended for blacks and browns, and sumach extract or peachwood for light colors. The amount of mordant depends largely on the color, larger quantities being necessary for black and dark browns than for light shades. About 2½ to 4 per cent can be generally recommended.

The best method is to drum the goods in an infusion of the tannin at a temperature of 110 deg. F. for half an hour. At the end of that time the goods should be taken out of the drum and placed in the vessel in which they are to be dyed. After working for 5 minutes in warm water at 120 deg. F., the basic dye solution (filtered) containing acetic acid should

be added in two portions and the goods drummed for half an hour.

Fat-liquoring can then continue in the usual way.

Dyeing with Direct Dyes

These popular cotton colors have a great affinity for chrome and may be used in the same way as acid dyes, only they require no acid to develop the color. The best temperature for the dyebath is 135 to 140 deg. F.

They may be used with acid colors with great success to obtain better penetration and, when the former are used, there is no need to add any acid.

Direct colors are especially recommended for box and willow calf intended for shoe uppers, but they are not so suitable for glace kid or full chrome sheepskins. Kid is best dyed with basic colors, and chrome sheepskins with either basic or combinations of acid and basic.

Good Blacks on Chrome Leathers

A combination of direct chrome blacks and acid blacks can give satisfactory results without the use of any mordants, and by the use of this method it is possible to obtain very full blacks in the most economical and simplest manner.

When acid dyes are used alone to obtain blacks, then the latter should first be mordanted with logwood extract, 3 per cent on the shaved weight. It is advisable to add the acid dye fifteen minutes after the addition of the logwood and to drum for a further thirty-five minutes.

Where there is any chance of the fat-liquoring stripping some of the black, then it is advisable to add the former immediately after the dye. Direct colors are less affected by alkaline liquors than any others.

Skivers

Practically all light leathers, such as skivers, basils, roans, goats, light hides and calf, are tanned by total immersion in a solution of dye; heavier leathers are stained by hand with concentrated solutions of dye.

The general procedure in the case of skivers is to wet them down in warm water, temperature 110 deg. F., for ten minutes, then to process them in a paddle with an infusion of sumach made by adding 5 per cent of best Sicilian ground leaf. After twenty minutes they can be taken out of the paddle, rinsed through cold water to remove pieces of sumach, and then after draining for a few minutes, thrown into the dye paddle containing only warm water, temperature 115 deg. F.

This preliminary process which necessitates two separate operations, is not, of course, absolutely essential and may, where the expense cannot be justified, be omitted. There is no doubt, however, that when sumaching is undertaken immediately before dyeing, it does materially help in the even absorption of dyes and the formation of brilliant color lakes.

The procedure of dyeing skivers is very simple. First of all, the skins are paddled in water at 115° F. for three or four minutes, then one-half the amount of the stock solution of acid dye added, and after a few minutes, half the amount of acid necessary to develop the color. At the end of 15 minutes, the remainder of the dye, followed shortly afterwards by the acid, should be added, and dyeing continued until a total time of half an hour has elapsed.

After dyeing, the goods should be lightly rinsed in cold water, and then struck out by hand or machine, and strained on frames or boards in a moderately warm stove.

In the case of skivers for hat bands or linings, special care

has to be taken to prevent any looseness of the color and to reduce to a safe minimum its inclination to rub. It is advisable to use only the best dyes for this work, preferably those which are not very toxic or liable to poison the skin of anyone wearing a hat lining dyed with the particular color. As some dyes are considerably more poisonous than others, this precaution is worth while. The dye manufacturers will usually be found very willing to collaborate in working out safe and economical recipes for special purposes where any extra cost involved will be thoroughly justified.

The method recommended by Flemming in his book on "Practical Tanning" is very suitable for the preparatory treatment of skivers intended for hat linings. He states:

"The quantity of sumach (3 lbs. for 225 average skins) is mashed with hot water, then added to lukewarm water in the paddle, and the skins are thrown in and run for one hour, and then taken out and set out. . . . The next process is the treatment with fustic extract and titanium salt. For 100 lbs. of leather, 1½ pints of fustic extract is dissolved and added to warm water and the skins are drummed with the liquor twenty minutes. Half of the titanium salt dissolved in a little hot water is then added, and five minutes later the rest, and at the end of fifteen minutes the leather may either be colored and fat-liquored, or fat-liquored first and colored afterwards."

To fasten the color of these special skivers, it is advisable after dyeing and before rinsing to draw them through a tray containing a weak solution of potassium bichromate, ½%, temp. 110° F., will be enough. This powerful oxidizing agent seems to darken the color slightly and it is, therefore, advisable to watch this point carefully, especially when working with light shades of brown. Bichromate has an injurious effect on vegetable-tanned leather if allowed to remain in contact with it too long. Generally speaking, skivers

do not need any fat-liquor, but it is a wise precaution to add a small quantity of sulphonated olive oil, 1% on the dry weight is ample, to the dye bath at the completion of the process.

Roans and Basils

The procedure for these does not differ very much from that recommended for sumach skivers. In the first place, the goods have to be trimmed in the crust warehouse, then sorted for colors, blacks and printed or embossed grains. Some of the skins may require degreasing and, if there is a petroleum degreasing plant on the premises, the grease should be extracted in the usual way. However, some tanners do not think very highly of the petroleum extraction process and are of the opinion that it is too severe and leaves the leather impoverished; for this reason they prefer to use one of the new mild fat solvents which can be utilized in a drum or paddle, preferably the former, in aqueous solution.

A large proportion of the heavier sheepskins require shaving and these must be wet down in cold water, placed on a horse and allowed to sam; they can then be sorted by the charge hand who should make three or four piles; light necking, necking, backing, heavy backing. Shaving follows in the usual way.

All shaved leathers must be cleared to remove all traces of iron, due to particles of grinding dust which invariably attach themselves to the flesh side. A solution of dilute vitriol is the only really satisfactory one for clearing and removing iron stains, no stronger than 2% should be employed. A wise tip is to use a small amount of both sumach and neutral salt, such as sodium acetate, in the sour liquor. A working formula would be a 1½% sulphuric acid solution, 10 lbs. sumach, 4 lbs. sodium acetate, temperature 100° F., for a pack of 20 dozen skins.

If any stripping is necessary before clearing, then this should be carried out with some safe alkali, such as borax, about 1½%. The action of this alkali is very mild and it has no injurious effect on the grain of the skins, which it leaves soft and silky. The action of alkali is to remove all loose tannins, dark coloring matters from certain tannin bodies, and grease. Usually, borax will saponify a good deal of the dressing oils, such as sesame oil, which is frequently found in E. I. Persians and goatskins, but it cannot be relied upon to remove the heavy and very complex animal fats, the presence of which is only too easily detected in heavy English sheepskins, which often show the back and neck sodden with grease.

The best procedure for light stripping is to drum the goods with 1½–2½% on the dry weight in just sufficient water, temperature 115° F., to process goods nicely. Fifteen to twenty minutes is a safe average time and, at the end of that time, the liquor should be run out of the drum and the goods washed in running cold water for fifteen minutes. They can then be cleared, sumached, struck out, if necessary, and dyed. Some tanners like to strike out goods, both before and after dyeing, as in their opinion it enables them to obtain a uniform or level dyed surface, free from creases and wrinkles. The extra cost involved for this additional process would not, of course, be justified for any but the most expensive goods.

Drumming in a warm sumach liquor is always advisable, and in the case of stripped goods it is absolutely essential to replace the tannins lost during stripping. About 5% of sumach on the dry weight of goods is recommended. A small percentage of sulphonated oil can be added without detriment to the subsequent dyeing process.

General dyeing procedure does not differ very much from that recommended for skivers. Roans or basils may be dyed

with equal success either in the paddle or the drum; the former is preferable if the grain is to be kept as smooth and soft as possible, although it is somewhat more expensive.

Vegetable Tanned Goatskins

In Europe the majority of the vegetable tanned goatskins are E. I. goats which arrive in the crust state from India. They are well tanned, fine textured skins which, in spite of their high price, have for many years proved most economical to the tanner. There is practically no offal and the tannage is so light and uniform that almost any color may be dyed with comparative ease. Most of the skins require a certain amount of shaving, then follows clearing, sumaching and dyeing with acid dyes in a drum at a temperature of 115–120° F.

Fat-liquoring with sulphonated oil and soap is recommended for all vegetable-tanned goatskins, which are mainly used for morocco and colored or black glace for shoes and slippers, as well as fancy trade work.

The proportion of fat liquor should be kept as low as possible: 5 lbs. sulphonated olive oil, 5 lbs. sulphonated castor oil, 2½ lbs. Castile soap, 1¼ lbs. egg yolk, represents a workable formula.

Dissolve the soap in 5 gallons of boiling water and add the two lots of sulphonated oil. Centrifuge, and then when solution is at blood-heat, add the egg yolk and centrifuge again until a perfect emulsion is obtained. This liquor makes an excellent fat-liquor for vegetable goatskins and it is sufficient for processing 25 dozen medium E. I. goatskins, which, after all, require but little fat-liquoring.

Vegetable Tanned Calf and Light Hides

More generous shaving is generally necessary with this heavier class of work, so as to insure a uniform cutting area

for the shoe or bag manufacturer. It is, however, a grave mistake to shave down the substance of the skin to fit in with micrometer specifications. A wiser plan is to build up the order from a more suitable range of goods which only require slight necking or other adjustment. Too much reduction of substance by means of the shaving machine is not only expensive, but it is definitely weakening to the leather and renders it quite unfit for many purposes where a tough leather is required.

To facilitate wetting down for shaving or wet processing, it is advisable to make use of a small proportion of a good chemical assistant in the form of a suitable sulphonated alcohol or ester, such as Betasol O T, which belongs to the latter type. If the crust goods are wet down in a drum containing a 2½% of a reputable wetting back agent, a considerable saving in time will be effected and the leather will respond very much better and easier to subsequent processing.

After clearing in a weak solution of sulphuric acid containing sodium acetate, the goods should be drummed in sumach or sumach extract and subsequently dyed in the drum with acid dyes. A small proportion, say 1% on the dry weight of goods of the wetting back agent, will help to insure level coloring and improved penetration.

A larger percentage of fat liquor is necessary than that advocated for goatskins and the proportions for the latter given should read for 10 dozen skins, either medium weight calf or light hides.

Fat Liquoring Light Leathers

Fat-liquoring is one of the most vital operations in leather manufacture as it is upon the efficiency of the process that

the feel and appearance of the finished leather as well as its strength and ability to resist the penetration of water depends. Too much fat, particularly if it is sulphonated, makes the leather cloth-like, or even raggy, and liable to throw off the excess in the form of spue, and too little will cause it to dry out harsh and to crack when staked or finished in the ordinary way.

Some light leathers, such as skivers and very light roans, require little if any fat liquor, as the tannage, especially if it is sumach, gives an exceptionally soft natured leather. In the case of vegetable tanned leather which is degreased by the solvent extraction process, a small amount of sulphonated oil is sometimes advisable as an addition to the dyebath, but it is not absolutely essential. Where fat-liquoring is absolutely essential, although it is possible to use an alternative method for at least partial substitution, is in the processing of chrome tanned leathers.

It has been said that the real purpose of fat-liquoring is to lubricate the fibres of the leather and so allow them to move over one another both freely and easily. This is, however, by no means its only function and recent research appears to indicate that fat emulsions cause a splitting up of large fibres into finer ones. A. A. Pchelin & E. I. Ginzburg (Tsentr. Nauch-Issled Inst. Kozhevennoi Prom, Sbornik Rabot, No. 9,120 [1936]) consider that fatty substances, being surface active, cause the splitting up of large fibres to become irreversible and so increase the breaking strength of the leather. The softness of the finished leather is in their opinion dependent upon the degree of division of the large fibres into small ones. Their work has so far been mainly concerned with chrome leather, but many of their conclusions may be said to apply equally well to other types of leather.

Most practical tanners will agree that fat-liquoring is a

complicated process and one that relies for its efficiency on several closely related factors. First of all there is the question of the condition of the goods. Thus when fat-liquoring chrome tanned leathers, the chrome content and degree of neutralization influence to a considerable degree the total absorption of fat. That is one of the reasons why it is so important to standardize all working recipes and so ensure perfect uniformity of results.

In the case of vegetable tanned leathers it is known that different tannages influence the fibres in their ability to absorb and retain fat from emulsions in different degrees and ways. This influence is due to the pH of the tan liquor, the astringency of the tannins present and the presence of neutral salts. When, however, buffer salts, such as sodium acetate are present in the liquors, the tanned leathers usually process more evenly than when those salts are absent.

The condition of the fat when it is absorbed by the leather also contributes a great deal towards the usefulness of the process. Dr. F. Stather in his interesting and valuable paper at the 1938 Copenhagen Conference of Leather Trades Chemists, stressed the fact that it is necessary to draw a distinction between the "absorbed," "extractable" and "combined" greases. Although the total quantity of grease taken up by chrome leathers is directly proportional to the quantity of grease used, the type of fat chosen for the purpose also influences the total.

According to Dr. Stather the quantity of grease taken up from the liquor by the leather is greatest from sulphonated oil fat emulsions, slightly less from soap fat liquors and considerably less from those made up largely or wholly of egg yolk. The quantity of combined grease increases rapidly with increasing degree of sulphonation of the oil; although when using sulphonated oils, particularly sulphonated castor oil, it is possible to obtain the maximum "combined"

grease content and in consequence a soft leather without achieving exactly the result desired. Perhaps a heavier type of oil is needed, or maybe the addition of some solid fat is required to increase the size of the fat particles in the emulsion.

For light leathers, such as skivers, roans and vegetable tanned goods generally, if fat-liquoring is thought to be necessary, then a sulphonated neatsfoot or cod liver oil is usually quite suitable, but in the case of chrome leathers the best result is obtained when a blended emulsion is employed containing soap. The object of adding soap is not entirely for its properties as an emulsifier but also to exert a chemical action on the chrome fibres by depositing an insoluble metallic soap.

Choice of fat is difficult, not only because of the conflicting claims of manufacturers handling proprietary brands of fat-liquors, but also because no two tanners agree on what is the best recipe for any particular grade of goods. The only conclusion one can arrive at is that it is possible to obtain excellent results with several different recipes, provided these are well balanced and of a type to suit the leather in question. Light goods should be given little, if any, free and unsaponifiable mineral oil, but this might well be incorporated with a heavy sulphonated cod in the case of chrome tanned goods.

It is not often realized that the presence of free mineral oil is most valuable as it helps to reduce the penetration of the sulphonated oil emulsion and does good work by penetrating the outer layer of fibres which are often not touched by the sulphonated oil. An excellent mixture consists of sulphonated cod or neatsfoot oil, medium grade light mineral oil and egg yolk. Some tanners have an aversion to sulphonated oils and much prefer straight emulsions consisting of soap, oil and, if desired, a small percentage of egg yolk. Their complaint against sulphonated oil is that it tends

to increase the liability of the leather to spue, makes the flanks raggy and often strips the color. While it is to a certain extent true that badly prepared sulphonated oils often contain high proportions of hydroxy stearic and elaidic acids which cause spue, it is possible to obtain supplies of oil containing the absolute minimum of these bodies. Egg yolk is always a useful additive when it is necessary to produce a soft leather with an exceptionally fine break and it may be used in conjunction with sulphonated neatsfoot oil.

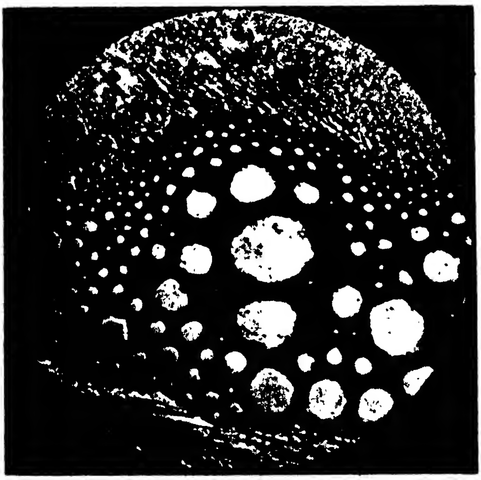
The size of the fat globules in the emulsion has an important influence on the efficiency of the process. Thus if they are too large there is always present a danger of lack of penetration and patchy results caused by oil spots on the grain. This latter fault may lead to uneven finishing and even spueing. On the other hand, if the dispersion of the globules is too great there is a risk that a good deal of the fat liquor will penetrate to the center of the leather, but leave the flanks loose and raggy. An acid fat liquor is always preferable to one on the alkaline side, as its stripping action on dyes is not so noticeable and it can, if desired, be used before dyeing.

Flemming, in his book on tanning, recommends the use of "sulphonated oil in conjunction with neatsfoot oil." He considers that "many of the difficulties of the fat-liquoring process can be overcome by using a fat liquor made as follows:

"Two and one half pounds neatsfoot oil are heated to 160 deg. F., together with ½ oz. of carbonated potash. Then add 12 ozs. potash soap dissolved in boiling water. Stir well, shut off steam and add ¾ lb. sulphonated oil. This forms an emulsion that mixes readily with water. Use about 3 per cent of this mixture (for chrome calf) calculated on the weight of the leather after shaving."

Eitner does not consider neatsfoot oil an ideal ingredient of fat liquors as it contains tallow which is liable to spue out

of the leather. In his opinion olive oil and olive oil potash soap are the most suitable for general use. On the other hand, recent experiments carried out by A. A. Pchelin and E. I. Ginzburg (Tsentr. Nauch—Issled Inst. Kozhevennoi Prom, Sbornik Rabot, No. 9,200 [1936]) indicate that when sulphonated neatsfoot was used in conjunction with raw neatsfoot oil, mineral oil and soap, in 5% emulsions having a pH 6.5—8.0, excellent results were obtained. Their recipes were made up as follows:



PHOTOMICROGRAPH SHOWING FREE OIL GLOBULES IN A BADLY PREPARED SOAP AND OIL EMULSION. . . . THE GLOBULES HAVE FLATTENED OUT TO BECOME SEMI-DRIED DURING THE DRYING OF THE SPECIMEN ON THE SLIDE. (PHOTOGRAPH BY THE AUTHOR.)

Sulphonated neatsfoot oil	30	25	20
Neatsfoot oil	40	30	40
Mineral oil	20	20	20
Soap	10	25	20
	100	100	100

Some attention has recently been given the merits of phosphatized oils, but so far they have proved rather disappoint-

ing. U. S. Patent 2,079,973 covers the production of water soluble sulphonation products of the phosphatides which comprises treating the phosphatide with a sulphonating agent in quantity at least equal to 60% of the weight of the phosphatide. Washing, wetting, emulsifying, dispersing, cleaning and softening are possible with these new materials which are freely soluble in water and have, it is claimed, high permeation and penetrating powers, stability to acid, insensitiveness to lime and high protective colloidal value.

The writer considers that some of the new washing detergents of the Gardinal or Igepon type should prove useful additives for special fat liquors, but they cannot be entirely substituted for soaps in the case of chrome leathers. One great advantage of these new synthetic products is that they are completely unaffected by hardness of salts in water and the pH of the solution or the leather itself.

The three ethanolamines of which triethanolamine is the most important, are of considerable interest to the tanner. Triethanolamine is a viscous and colorless liquid possessing a slight ammôniacal smell. It combines with free fatty acids in molecular proportions to form soluble soaps having a pH of about 8. The ethnolamines are excellent emulsifiers and stabilizers and their soaps might well be substituted for ordinary curd soaps in the preparation of blended fatliquors for chrome goods. Triethanolamine oleate is particularly suitable when used in conjunction with a heavy mineral oil and sulphonated cod. E. R. Theis & F. S. Hunt (Ind. Eng. Chem. 1, 1931, 50) found that when triethanolamine was added to fat liquor, much less oil was needed to give good results and the time necessary to complete the process was reduced. In their opinion the emulsifying properties of triethylanolamine wefe effective if the raw oil used had a high acid value.

The value of egg yolk in fatliquoring recipes, particularly

Scraper device recommended for the efficient mixture of fat liquors; especially those consisting of hard soap, free oil, and water. (Courtesy Sowers Mfg. Co., U. S. A.)

for glace kid and gloving leather (chrome or alum goods) is now well recognized and appreciated by tanners. The active component of the yolk responsible to a large degree for feeding properties of these emulsions is lecithin. During recent years various attempts have been made to isolate lecithin from soya bean and to use it as an additive to commercial fat liquors. The idea seems very promising especially as the separation of lecithin offers no great technical difficulties. Besides improving the handle of dressed goods, lecithin (according to W. Schindler Coll., 1936, 77) retards the oxidation of the fat in chrome leather during storage or use and to a great degree reduces the risk of resinification and also spueing, when vegetable oils are used.

In any discussion of fatliquors, consideration must be given to the question of spue. Procter puts it down to the crystallization of hard fats present in the oil, especially of the free fatty acids. He says that it "is almost sure to occur in greater or less degree when the hard fats such as tallow or stearine are combined with a non-drying oil such as neatsfoot or when soft fats are present in the leather." Procter mentions that Eitner (Gerber, 1880, p. 243) "states that seal oil extracted at low temperature is very liable to spue, but that when heated for a considerable time to a temperature of 250 deg. to 290 deg. C., it darkens in color and loses the tendency."

The present writer considers that there is always danger if the fats contain free fatty acids, particularly stearic and palmitic, or if free fatty acids are formed as a result of changes which take place during the ageing of the fats in the leather. What has not yet been fully explained is why these solid fat acids which are present in five out of six oils, do not always crystallize out on the grain. Agencies are at work to accelerate spueing which are not yet recognized. The presence of free mineral salts has, in the writer's opin-

ion, a great influence on the formation of spue in chrome leather and that is why the latter should be very thoroughly washed after neutralization.

There are some proprietary fat liquors which contain a very high proportion of their fatty acids in the form of oleic acid, which is by far the safest of the series, and also less liable than stearic or palmitic to leave the leather with a greasy surface.

Setting-out or Striking-out

After dyeing and fat-liquoring the next process is setting-out or striking-out, which today is usually done by hand. After removing excess liquor from the skins and also smoothing away wrinkles, the goods are placed on wooden horses and removed to the drying sheds. Practically all dyed goods are strained, but whereas a few years ago there was only one method available, namely to tack the leathers on wooden boards held in racks in large steam-heated stoves, today there are several ways the tanner can dry out his dyed goods.

A modern alternative to the standard method of straining on wooden boards is to stretch out the skins by means of toggles on to large steel mesh frames or mattresses. The advantages claimed, and indeed well substantiated, by those who favor toggle drying, are that there are no nail holes and no objectionable iron stains. Most of the better class toggles are made of a light but strong aluminum alloy and weigh about 16 to 18 to the pound. In general practice the toggle method of straining is fairly easy to learn and results in an increased area of leather, freedom from nail holes and stains, considerable acceleration in the time of drying and also freedom from the springing of goods off the frames owing to the firm grip of the toggles, and a better shaped skin.

The disadvantage of toggle drying on steel frames is that the initial expense in equipping the sheds with frames is liable to assume formidable proportions and some of the systems in common use are by no means foolproof and do not stand up very well to abuse. In addition, unless the frames are made of stainless steel (18% chromium and 8% nickel) or Monel metal a slight staining often occurs which is sufficient to be noticeable. This staining may be due to the combination of metal with the dye or the effect of the metal on the actual fibres of the leather.

Apart, however, from the above disadvantages, there is no doubt that the toggle method of drying has much to commend it and is a great advance over the old method of tacking the skins on boards.

A method which is now becoming very popular in America is known as pasting and consists of setting out the leather on large plates of anodized aluminum, stainless steel, Monel metal or enamelled metal and then hanging those sheets in a specially designed drying tunnel where an average drying temperature of about 110° F. and an average relative humidity of approximately 60 per cent are maintained. Leather dries in this properly conditioned atmosphere in from two to seven hours depending, of course, on the type of leather treated and the conditions maintained. Systems are available which insure perfect scientific control of drying and are as near being foolproof as any method available so far. By altering drying conditions it is possible to obtain any desired result and provided the system is working properly there is no possible danger of skins falling off the sheets.

Where it is not a practical policy to invest in an elaborate and costly drying system, the tanner can do a great deal to improve his drying sheds and make them more economical and efficient. In many tanneries the works manager has to struggle against heavy odds in the form of badly designed

and unsuitable buildings and equipment. The old idea, and one which unfortunately is still rather prevalent, is that drying-sheds can easily be made by merely installing steam-pipes and suitable ventilating devices in large airy lofts provided with racks and hooks.

The result is that when these frequently unsuitable rooms are in regular use throughout the year all kinds of troubles crop up. For instance, if the roof is of galvanized iron the problem of condensation is sure to put in an appearance sooner or later, and condensation from such a roof invariably means iron stains due to the small amount of free and dissolved iron salts in the drops of cooled water. This trouble can only be overcome by covering the roof with a ceiling of asbestos wallboards or other fire resisting and insulating material. Another important fault to be found in many drying rooms is that heat losses through walls and roofs are often excessive and mean that the heating system has not only to warm up the surface and the skins, but also the surfaces of the surrounding walls.

It is strange that none of the text books on leather manufacture give much consideration to this question of heat insulation. The author recommends the use of aluminum foil for lining the walls and ceiling of the drying rooms. The high insulative qualities of this material depend upon three of the fundamentals of physics—that radiant heat "bounds off" a shiny metal surface and is therefore not readily absorbed thereby—that a bright metallic surface is a poor emitter of radiant heat, and that air is a superior heat insulator. Heat insulation in buildings by means of aluminum foil (preferably in a reinforced form) may be expressed as depending upon the scientific combination of the following factors:

(a) The low emissivity for radiant heat possessed by a bright metallic surface.

(b) The high reflecting power for radiant heat possessed by a bright metallic surface.

(c) The low heat-conducting properties of air.

(d) The hindrance to the passage of heat by convection currents offered by an air proof material such as the foil when properly fixed and spaced.

Of the metals, aluminum is the one which next combines the essential qualities of low emissivity and high reflectivity with the lowest degree of thermal capacity, the greatest surface stability and a ductility permitting of the rolling of very thin sheets. Furthermore, while most metals tarnish in the air, with consequent increase of emissivity, aluminum forms a very thin oxide coating which protects it against further attack and does not appreciably increase its emissivity.

Drying rooms can be efficiently insulated with aluminum foil by merely lining the walls and ceiling with sheets of the reinforced variety and then covering the foils with asbestos cement rough sheets so as to leave a still air space between the outer surface and the shiny metal diaphragm. This method will not only prevent heat losses but will accelerate the whole process of drying and by the conservation of heat cut down heat losses to an absolute minimum.

Control of the drying system depends to a large degree on the proper use of thermometers. The most generally serviceable type is, of course, the wet and dry bulb thermometer, by which it is possible to determine the relative humidity of the atmosphere. By watching this instrument the foreman should be able to tell exactly the condition of drying out at any particular time, and if the readings are kept constant so that evaporation of moisture is maintained at a predetermined rate, then uniformity of drying will be assured.

For convenience tanners are advised to use a modern hygrometer chart instrument which will show graphically the relative humidity, dew point, absolute amount of moisture

present, and the weight of water in each cubic foot of air, expressed in grains. In addition to the wet and dry bulb thermometer there should be a wall thermometer in use, and also a portable thermograph available for occasional records of temperature variation during any one night or day period. The bimetallic coil type of thermometer is the most sensitive and generally serviceable.

To check up the temperature of the steam coils it is a good plan to make use of a pipe type of thermometer where the element is in close proximity to the pipe and has a range from 32° F. to approximately 330° F. It is a good practice for the foreman in charge of the drying sheds to be instructed to record temperature and humidity readings on the order card attached to each batch of goods. This data, if reliable, can be of the greatest help to the works manager in helping him to explain why one batch of goods is in a better condition than another. For instance, experience shows that the color of dyed skins dried out too slowly is liable to be patchy, and it is, of course, known that quick drying makes leather hard and biscuit-like.

Drying

In drying, as in many other processes, the goods have to be humored to give the best results. Some leathers will stand forcing, others respond very badly. Although it is a general practice to strain goods after dyeing, some tanners in England find it a better plan to adopt a different method for full chrome clothing and gloving leathers. After setting, the leathers are merely hung up in warm stoves and allowed to dry out overnight, then next morning they are taken down and placed in damp sawdust to condition ready for staking. When properly softened by machine they are immediately strained and allowed to dry off in a hot stove. This rathe·

cumbersome process is found to give excellent results and although it entails extra labor charges appears to be worth while.

When it is desired that the goods should condition easily after drying, it is usual for the set out goods, and especially chrome calf, to be sponged over very lightly with a weak solution of glycerine. This is hydroscopic and absorbs moisture very readily.

The draught through the sheds influences drying to a considerable degree and that is why it is so important to install the right kind of fan. The type and size must depend largely on the size of the room. Procter in his "Principles of Leather Manufacture" gives valuable guidance regarding the most suitable kind of fan to use. He writes:

"Screw-fans are rather advantageous where the fan blows into an open room, but involve waste of power where it discharges into narrow and square airways . . . Screw-fans are good for moving large volumes of air at comparatively low velocities and against little or no resistance, but they are quite unsuitable for forcing air against high resistance or through narrow channels, and for this purpose centrifugal fans are much more suitable and mechanically more efficient. In any case there is much loss of power in forcing air through narrow airways and if a screw-fan must be employed for the purpose, the channel should be as large in section as the area of the fan, and all sharp angles in its course should be avoided."

To test the efficiency of the fan it is advisable for the tanner to make use of an anemometer which will record low wind speeds and so give reliable data regarding the velocity of the current set up by the fan, either blowing or sucking. In many important tanneries the writer has observed that the tendency is for the management to consider that drying, except where automatic systems (like the Bristol) are in-

stalled, is a simple process requiring the minimum of skilled attention. The result of this negligent treatment is that batches of goods vary considerably in condition and drying times become uncertain owing to the vagaries of the weather.

In the writer's opinion only the best and most uniform results can be obtained by intelligent supervision of drying and the foreman in charge should not only be able to get the best out of his heating and ventilating apparatus, but exploit to the full the recording instruments which he has at his disposal. Another point often missed by tanners is that weather forecasts are vitally important and should be noted and taken into consideration by the foreman. If he learns that rain or cold winds are expected following a warm, dry day, then he should make suitable allowances by turning on a little extra steam and reducing outside ventilation (usually in the form of louvres) to compensate for the difference in temperature and humidity between the interior of the shed and the outside.

Reliable weather forecasts, and meteorological readings are now becoming fairly exact for short periods, and knowledge of these is a valuable asset when properly exploited. Other factors contribute a great deal to the success of the whole process of drying in ordinary stoves. Nails should not be allowed to get too blunt, otherwise they make large holes in the leather, sometimes even tear it, and in many cases they are unable to resist the stress and pull of the contracting leather during drying and so are pulled out. Nails are cheap and it is false economy to husband them too carefully. Boards also should be renewed when they become badly pitted and no longer able to hold the nails. Mallets that are badly worn are unsuitable tools because the strainer finds it difficult to hit the nails squarely on the head and in consequence he drops a large proportion of nails on the floor. These are little points which merit consideration because in

works practice they assume a considerable degree of importance.

Fireproofing and Mothproofing Leather

The term fireproof is really incorrect, as it is impossible to make an organic material really fireproof. Even such an inert inorganic material as asbestos cement is no longer called fireproof, the term fire resisting being generally preferred.

Leather does not naturally burn easily; first of all, it chars, swells and finally burns with a feeble blue flame. The fierceness of the flame depends, of course, on the nature of the leather burned. Mineral tanned leathers do not, as a general rule, catch fire as easily as those tanned with vegetable tannins or oil. The presence of inflammable cellulose lacquers introduces an added risk and a heavy surface coating would naturally make leather burn both quickly and readily.

Attempts to make both textile material and leather, particularly the former, resistant to fire, have been numerous, although not always successful. Methods have generally consisted of impregnating the material with salts which on the application of heat give off an inert gas, such as carbon dioxide, or under the same conditions from an unpermeable glaze on the surface.

Most fire retardants and flame proofing agents contain one or more of the following chemicals: ammonium chloride, ammonium carbonate, ammonium phosphate, ammonium sulphate, borax, boric acid, dibasic sodium phosphate, sodium tungstate, lead acetate, sodium aluminate, sodium stannate and zinc sulphate. Recent experiments have greatly enlarged the field and such chemicals as borophosphate, a "resinous" body which dries out as a smooth, glossy and transparent

film, are meeting with some success for textiles, although no data is at hand regarding their application to leather.

A recent British patent, 483,153, taken out by N. Pal and Palsales, Ltd., covers a process which gives a glazed, fire resistant coating consisting of an underlayer of a soluble silicate covered with a coating of chlorinated rubber. The silicate may be applied as a pigmented solution and, after drying, coated with a solution of chlorinated rubber in xylol, mixed with tung oil. Resins or other oils may be added to either or both silicate solution and chlorinated rubber solution. The dried coating may be finally treated with an oil paint, varnish or enamel.

Certain metallic soaps, particularly aluminum stearate, have the property of resisting heat and are, therefore, often used for so-called fireproofing. Aluminum stearate is made by treating stearic acid with caustic soda to produce the sodium soap and then precipitating the aluminum stearate by the addition of a solution of aluminum acetate or sulphate at 110° F. The metallic soap is separated by filtration, pressed, and the cake, containing about 60 per cent moisture, dried in a current of hot air.

It is claimed that if a 2 per cent solution of aluminum stearate dissolved in petroleum is sprayed on the leather, the latter is rendered moderately flame proof, provided, of course, all traces of the solvent have evaporated. Unfortunately, the presence of aluminum stearate on top of a finish would disturb the gloss and tend to make the color slightly uneven. If used on the unfinished leather the same disadvantages would not apply, but if the leather were to be glazed the tool would stick and so cause trouble.

The formation of an insoluble aluminum salt in the fibres of the leather after tanning is advocated by some workers, and M. C. Lamb has taken out a patent, No. 465,533 to protect a method of making vegetable tanned leather fireproof

by treating the fully tanned leather which has been freed from grease or oil, with a soluble aluminum salt and then with a chemical substance which will form an insoluble aluminum compound in the pores of the leather. According to an example given by Mr. Lamb, leather is first drummed with aluminum sulphate and then with the addition of sodium phosphate. The Provisional Specification describes also the use of oxalic acid as a precipitant.

Aluminum formate appears to have interesting possibilities for this purpose, although it is better known as a waterproofing agent. This substance, which is becoming fairly well known in some industries, consists of a white, finely crystalline solid which, although only slightly soluble in cold water, is very soluble in hot. Thus at 20° C., only 50 grammes will dissolve in 1000 ccs. water, at 100° C., about 500 grammes will be taken into solution.

When leather is treated with soluble aluminum formate and then dried, the salt is converted into the basic insoluble formate which is completely inert and forms a glaze on the surface. As far as the writer knows, this comparatively new chemical has not been tried out to any extent in the tannery, but it certainly deserves consideration. A suggested method is to treat chrome leather with a 10 per cent solution of the triformate, temperature 45° C., after neutralization and before dyeing. The use of water soluble synthetic resins is worth considering as fire retardants. The amino resins are particularly well worth attention, as they are colorless and perfectly inert. These resinous bodies can be made quite simply by boiling urea with formaldehyde for 3–5 minutes until a soluble resin is formed, but not long enough to convert it into an insoluble, polymerised resin of the type used in the plastic moulding industry.

Chrome tanned leather can be treated with a 10–15 per cent solution of the neutral resin without in any way disturb-

ing its characteristics. If the leather is finished by hot pressing, the resin is converted into an insoluble form and so rendered still more inert. Another method of using these soluble resins is as a top finish which can be dried and given a semi-lustrous glaze by means of a Sheridan hot press.

Other organic chemicals have been tried out as fire retardants and the reader is referred to an interesting English patent, No. 476,043, taken out by the Bayerische Shckstoffwerke. The inorganic borophosphate Abopon, is also a good flame proofing agent when applied in aqueous solution, but does not appear to have received much consideration.

Mothproofing leather has now assumed a certain amount of importance, although many firms are very chary about treating expensive leather with chemicals, the properties of which they know very little. There is, of course, always the danger of the soluble salts spueing out or affecting the color or handle of the leather. The best known chemicals for use as moth retardants are the sodium silicon fluorides and similar compounds and their use for this purpose is covered by a number of patents both in Europe and America. Judging from experimental results these fluorides are very successful and appear to endow furs and textiles with excellent immunity to the attack of moths.

A number of patents have also been taken out to cover the use of many new and extremely complicated organic compounds. The I.G. Farbenindustrie Akt-Ges is responsible for several patents. Thus B.P. 466,344, Aug. 22, 1935, mentions a product obtained by reacting monomeric propylethyleneime with epichlorohydrin as a preservative against moths. Another patent taken out by the same concern, B.P. 483,368, Sept. 14, 1936, states that fibrous material of animal origin, such as textiles, hides, leather, furs and feathers, can be protected from attack by moths and other pests by incorporating therein an aromatic or heterocyclic compound

having a substituent containing at least one quaternary nitrogen atom. Preferred compounds include those made by reacting diphenyl derivatives, e.g., 4- hydroxy or 4- aminodiphenyl with monochloro-triethylamine or 1.3- monochloroproplylamine.

The substances may be employed in solution in water or organic solvents and the treatment applied during dyeing, fat-liquoring, degreasing, etc.

Another interesting patent, taken out by Geigy Aktges, B.P. 471,404, Dec. 14, 1936, covers the use of amides of aminocarboxylic acids. In the examples quoted by the patentees, dimethylaminoacetic acid N-lorylanilide ("loryl," meaning the radicle of the mixture of higher alcohols obtainable from cocoanut oils) is prepared from dimethylamine and chloracetic acid N-lorylanilide and converted into salts with mineral and organic acids.

VI

FINISHING

DURING the last ten years great progress has been made in the manufacture of water bound pigments and these can now be trusted not to clog up the grain of the leather; and give it a uniformly flat and paint-like appearance. The aim of the modern finisher is to preserve as far as possible the natural looks and handle of the leather and yet at the same time even the color and cover up such defects as weak grain, scars, etc.

Tanners seldom make up their own dope and it is usually purchased in drums from firms specializing in the manufacture of leather finishes. Most of the proprietary lines consist of pigments suspended in alkaline solutions of casein and shellac containing sulphonated oil and other plasticisers.

REQUIREMENTS OF PIGMENTS

A great deal depends on the condition of the pigments and M. C. Lamb, J. Soc., L.T.C. 231–238, 1929, has ably summarized the main requirements of pigments suitable for use in the manufacture of water bound pigments.

1. The pigment should have been ground into the finest possible colloidal condition in order to minimize the liability of rapid sedimentation when the pigment is mixed with the aqueous solution of the binding agent, so as to keep it in a state of suspension for as long a period as possible.

2. The pigment must be reasonably fast to light.

3. As the more commonly used binding agents require the use of a weak alkali in order to effect solution, the pigment chosen should be unaffected when mixed with an alkaline medium for a long period.

4. The pigment should not be affected by the application of heat such as is experienced when the leather is hot-plated on an ironing or embossing machine.

5. It is essential that the pigment should possess good covering power when it is used in a comparatively weak mixture.

6. The pigment should be colloidal and not granular, so as to ensure imparting the necessary soft, smooth feel to the leather upon which it is applied.

7. It is important that the pigment should be unaffected by any atmospheric influence to which the leather may be subsequently subjected, as, for example, lead salts and their liability of becoming darkened by exposure to sulphuretted hydrogen.

8. The pigment should contain no soluble salts, and especially is this necessary in the case of those known to possess poisonous characteristics such as lead and chromium.

Favored Method

The method favored by some English dope manufacturers is to grind the pigments with a suitable grinding base in ball and pebble mills. The colors to be ground are placed in a suitably lined cylinder or barrel in which is placed a quantity of flint pebbles, porcelain or iron balls. The mill is mechanically revolved and the pebbles or balls, rolling over and rubbing together and against the walls of the mill, eventually reduce the material to a fine powder. The degree of fineness is determined by the length of time occupied in the

grinding. For the very best finishes the pigment is ground in a ball and pebble mill and then reground in a two-roll mill or Banbury mill with a suitable grinding base such as casein, glue, methyl or ethyl cellulose. The two latter materials are particularly advantageous for grinding oxidizing pigments, such as iron blues and chrome yellows, etc.; the time of the first grinding influences, of course, the degree of grinding necessary in the second case.

The aim of the manufacturer, no matter what method of grinding he employs, is to produce a colloidal form of the pigment which can be suspended in the medium for an indefinite period and which will give an easy flowing liquid.

The fastness of a water-bound pigment dope depends on a number of factors which deserve consideration at this stage. First of all, there is the actual composition of the finish. It is known that some pigments are given to chalking and tend to render the film less resistant to rubbing. Titanium oxide is inclined to be troublesome in this respect and care should be taken to see that, instead of using the pure oxide, a co-precipitated titanium barium pigment is employed. Such a white pigment is naturally less affected by solar radiation than the pure oxide. Then there is the question of the adhesive property of the binder. This is most important and depends to a degree on the penetration of the finish in the grain of the leather.

Penetration

Although it is not desirable that the leather should be wetted to any great extent, it is essential that the finish should sink in a little and so make a firm grip. A. S. R. Rundle, Le Cuir Tech., 27, 82, 98 (1938) considers that the degree of penetration depends upon viscosity and surface tension. The proper dispersion of the mineral pigments de-

pends upon the viscosity of the solution. He also states that changes in viscosity are not due to changes in pH, but to fundamental changes in the constitution of the solution. In solutions used for finishing, the casein acts as an acid, forming caseinates of sodium, ammonia or triethanolamine. The physical and chemical condition of the leather plays a vital part in influencing adhesion of the film.

It is, of course, a well known fact that greasy leather will not take a water-bound pigment and requires degreasing before treatment. The pH of the leather is also important and the ideal arrangement is to adjust the pH of the dope to meet the particular requirements of the type of leather to be dealt with.

The Binder

Turning briefly to the constitution of the binder or dispersing medium, it may be said that the composition of this varies considerably and it is not uncommon to find a dozen or more ingredients present. The real basis of the solution is, however, shellac and casein rendered suitably alkaline by the addition of ammonia or other alkali. It is interesting to give a few brief particulars about shellac. This is really the resinous secretion of a small insect or louse belonging to the family of "Coccidae." Some 8½ million million (8,500,000,000,000) female insects produce yearly in British India some 60 to 70,000 tons of sticklac. When worked up into seedlac and shellac, the exported products amount to some 35,000 tons a year and constitute what is virtually a British India monopoly.

The Indian method of manufacture of shellac, as practiced largely today, is of interest and was given by R. Bhattacharya and A. J. Gibson, Nov. 24, 1938, in a lecture to the Borough Oil and Color Students' Association. After the

new generation of insects has left the lac incrustation (the process is known as "swarming"), the lac-bearing twigs are cut off, the lac is scraped off, ground, washed, dried and sieved prior to being filled into long canvas tubes of roughly five centimetres in diameter.

The Indian method of making shellac is actually a hot filtration process by means of radiant heat (a charcoal fire), the temperature being controlled by sprinkling with water. The filtered material is either cast into buttons to make the button lac of commerce or stretched into sheets, dried and broken up into flakes to form the shellac of commerce. The residue in the tubes is dissolved out with a solvent to make a dark shellac or is sold in its natural state as a residue lac or "kiri."

New Form of Shellac

A new form of shellac has, during the last year or so, been made available for use of leather finishers and it is proving very much more useful than the old hanks, flakes or powder which retain considerable quantities of moisture and frequently deteriorate on storing. The hanks of shellac are said to contain 25 per cent moisture and the powder and flake 5 per cent.

The new form takes that of needle shellac and it is manufactured by a patented process which may rightly be described as spinning from the molten or dissolved shellac. Long thin threads are thus obtained in a highly pure condition, containing very little moisture. The following advantages are claimed for the new needle shellac:

(1) It is a pure shellac containing no adulteration.

(2) It can be stored indefinitely without risk of deterioration.

(3) Blocking or coagulation does not occur.

(4) In the needle form it is more easy to dissolve than any other form, and concentrated solutions are rapidly obtained.

(5) The moisture content is guaranteed to be below 2 per cent.

(6) Drying and grinding of hank shellac is eliminated.

Shellac top coatings are in their pure form, that is made by merely dissolving shellac in methylated spirits, rather brittle and not suitable for many classes of leather where flexibility of the finish is essential. The usual practice is to add small quantities of glycerine or glycol, which has the property of softening the film.

Some tanners also add sulphonated mineral oil, which has a somewhat similar plasticising effect. The writer considers that a very serviceable and cheap top finish can be produced by adding 10 per cent ethyl cellulose to the shellac dissolved in methylated spirits, together with a little raw castor oil. This mixture may be diluted to the right consistency with industrial spirit and then lightly sprayed on the surface of the leather. If desired, the lacquer may be slightly tinted with a suitable spirit soluble dye.

It is only by skillful adaptation that the shellac lacquer can be made to give a smooth and flexible film which will give the leather a natural and genuine appearance. In most cases where shellac is used the results are by no means happy and, in consequence, the finished leather closely resembles a cheap artificial leather.

Water-bound pigments vary considerably in price, which is influenced naturally by the quality of the pigments and lakes used, their degree of fineness and the nature of the binder and emulsifier. It is false economy to purchase anything but the best finish and choice must be governed by experiment and study of the requirements of customers.

There are many occasions when dopes containing large

quantities of Carnauba, Japan or other wax may be desirable, as in the case of clothing leathers, but where the goods have to be glazed or rolled, a finish containing a larger proportion of casein is necessary. The tanner seldom knows, although he might make a shrewd guess, the true composition of the various dopes used, but he expects a general similarity in composition so that no snags are met with when he mixes them together to obtain certain color effects.

General Procedure

The general finishing procedure in most English tanneries is as follows: The goods are first staked and then placed on the tables, where they are brushed with a priming coating of the dope, which is nothing more than a fairly concentrated solution able to cover up weak grain and other blemishes and also even the color.

Brushing is advisable in the case of calk, kip and basils, but not necessary for skivers—as for these, a single spraying is usually sufficient. After brushing, the skins are padded off with a velvet pad, which causes the color to flow evenly over the surface and to smooth out all brush marks. When padded, the skins require drying at a medium temperature and then fluffing or stoning, which, besides cleaning up the flesh, has a decided softening action.

The next operation is spraying with top finish containing only a small proportion of pigment, followed by a spray of formalin or chrome hardening agent. After airing off, the leather can be ironed, pressed or rolled according to requirements. Several firms are now spraying the doped goods with a thin nitro-cellulose lacquer, which gives the leather an excellent water-resisting finish. This is preferable to the use of shellac, although the former is considerably more expensive.

Acrylic Finish

During recent years aqueous dispersions of the softer acrylic polymers have proved useful in finishing morocco and high-grade fancy leathers, and it seems possible that such preparations may be used as a final coating for goods dressed with water-bound pigment dopes. The chief advantages of the new acrylic finish are:

1. Excellent adhesion.
2. Permanent flexibility.
3. Preserve the natural handle and appearance of the leather.

Dr. D. S. Frederick, writing in "Modern Plastics Catalog," Oct., 1938, on Acrylic Resins, says: "The unusual flexibility and elasticity of these polymers are evident from the fact that films extensible in excess of 1,000 per cent can be obtained without the use of plasticizers. On stretching, films exhibit a certain degree of plasticity, and do not snap back to their original form but require an appreciable length of time for recovery.

"The molecular weight (viscosity) of the acrylic resins has a great influence on their properties. Polymers of high molecular weight exhibit greater tensile strength and more rapid extension after recovery than do lower polymers of the same chemical constitution. In general, the adhesion of acrylic resins to most surfaces is excellent, with the softer polymers superior in this respect. The crystal clear color and permanence of the acrylic coatings are unexcelled. Three years' exposure to weathering and sunlight causes no discoloration, no loss of gloss, or no failure of any kind with the harder films. Acrylic resins show good heat resistance, withstanding temperatures as high as 350 degrees F. without discoloration."

Cellulose Lacquers for Finishing Leather

The modern nitro-cellulose lacquer is a complicated preparation consisting of at least five different ingredients; nitro-cellulose, synthetic resin, pigment, plasticiser and solvent. Each of these ingredients plays a most important part in influencing the properties of the resultant film, for instance the elasticity, toughness, tenacity, gloss, etc., can all be altered at will by varying the proportions of these main ingredients.

The mechanical properties of the film are, however, not only greatly influenced by the constitution of the lacquer, but also by other factors, particularly the thickness of the film, its moisture absorption properties and adhesion to the base, and also the effect of the base on the film.

It will at once be realized that these are highly variable and difficult to control. In referring to the two important constants of distensibility and tensile strength, Dr. W. Krumbhaar in his book, "The Chemistry of Synthetic Surface Coatings," says that both constants govern the performance of surface coatings under practical exposure conditions.

"Distensibility of a coating may be measured in many simple ways while it is still attached to the support, for instance, by the ordinary bending tests of the Kauri reduction test. Other methods using impact testers or the Ericson machine lay special stress on the adhesion factor. Tensile strength determination are more difficult because they have to be carried out on the film detached from the support. The mechanical constant which is related most closely to tensile strength is abrasion resistance, high abrasion resistance, going with high tensile strength. Abrasion measurements, which can easily be carried out on the film attached to the

support are consequently often employed to take the place of the tensile strength determination."

NITRO-COTTON

Generally speaking three varieties of nitro-cotton are available—high, low and medium viscosities. The first named gives very thin films owing to the relatively low proportion of collodion cotton present even when the solution registers a high viscosity, and the other grades give correspondingly thicker films as the viscosity is lowered and the nitro-cotton content increases. For leather spraying it is usual to use a high viscosity cotton, but there are occasions when mixtures of high and low are needed.

While nitro-cotton and pigment are the two basic or foundation ingredients of the lacquer, the plasticiser is no less important because, as the name implies, it influences the elasticity (or plasticity) of the film, as well as other necessary properties. According to S. E. Sheppard and P. T. Newsome (J.S.C.I. 1937, 56, 256–261 T), plasticisers affect film properties by acting as coagulants or precipitants, probably by altering crystallite size. A large number of different organic chemicals are used today as plasticisers, but the two in most common use in the leather industry are blown castor oil the acid value not exceeding 1 to 2, and tricresylphosphate which appear to endow the film with the requisite degree of elasticity and light fastness, both essential properties. The use of castor oil compensates to some extent for the tendency of tricresylphosphate to turn yellow after long exposure to light and so alter the shade of delicate colors. There are several acetylation products of castor oil used as plasticisers, the best known being butyl acetyl ricinoleate. Another widely used plasticiser is di-butyl phthalate which produces clear

bright films with good elasticity and adhesion. It is very stable to light even when in contact with basic pigments.

A plasticiser which is now finding use in the preparation of nitro-cellulose and ethyl cellulose lacquers is hydrogenated methyl abietate. This is a complex product derived from natural resin acids by a chemical process which involves high temperature, high pressure esterification, followed by catalytic hydrogenation. The resultant product is a viscous non-volatile, water-insoluble liquid, pale amber in color, neutral in character and resistant to saponification by alkalies and weak acids.

As a resin plasticiser it helps to produce soft, but non-tacky, flexible films of relatively high tensile strength. Lacquers containing this material are resistant to temperature changes and also have advantages in moisture-resistance, flexibility and absence of surface tack.

Use of Resin

The use of resin in Nitro-cellulose lacquer is important because it tends to act in a similar manner to the plasticiser, improves adhesion and also the gloss, but its use in some leather finishes where glazing or hot pressing has to be carried out is not always advisable. The presence of resin in the lacquer must be influenced by the treatment to be afforded the leather after spraying, but where body and a certain hardness of finish is desired then a good quality, pale colored and easily soluble resin is recommended.

Dr. W. Krumbhaar states that "three different types of synthetic resins are in practical use with nitro-cellulose lacquer, that is to say the maleic acid types, the non-drying phthalic resins and the drying types of phthalics. The majority of these lacquers are made with half-second cotton, which is compatible with the resin groups mentioned. Sol-

vents are used in the customary way, their solvency power for the nitrocellulose being influenced by the resinous additions to a certain extent."

Choice of solvent, although apparently of minor importance, plays a vital part in the success of the finishing process. Usually solvents for nitrocellulose lacquers are divided into three grades: high boiling, medium and low boiling. It is seldom, indeed, that only one solvent is used and frequently as many as six or seven different diluents are used, which include the high boiling ethyl lactate or glycol monethyl ether, medium boiling butyl or amyl acetate and low boiling ethyl acetate.

Ethyl Acetate

Ethyl acetate is generally present in the best lacquers for both spraying and brushing because it helps to endow them with good flow, gives smooth, highly glossy coats and prevents blushing. It has a boiling point of 145–160° C. (95%) and a flash point of 125° F. and has a dilution ratio of 6.25 with respect to toluene and 5.7 to xylene. Butyl lactate, a high-boiling solvent of low volatility and very slight odor. Boiling point (95%) 180–202° C., flash point not less than 130° F. is preferable to ethyl lactate for brushing lacquers as it permits good flow. Where the goods are given a primary coat of nitro-cellulose with a brush, then this solvent is recommended.

Cyclohexanol and methylcyclohexanol are often used in association with ethyl lactate as high boiling solvents retarding evaporation and preventing blushing. The former boils at 158° C. to 163° C. and has a flash point of 155° F. Some of these hexanol products, particularly dimethylcyclohexanol oxalate and methylcyclohexanol oxalate, high boiling solvents approx. 180–200° C., are excellent plasticisers and im-

part great flexibility, adhesion and fine gloss to evaporated nitro-cellulose films.

In the preparation of nitro-cellulose lacquers the price factor unfortunately enters into the composition of the solutions and often rules out the presence of expensive high boiling solvents, with the result that difficulties are encountered, such as clouding, matting, poor flow, etc. A reasonable percentage of high boiling solvents, 10%, and the presence of such diluents as ethyl lactate, enables one to employ the maximum amount of hydrocarbon without danger of precipitation during the drying of the film.

Ethyl Cellulose

Comparatively recently ethyl cellulose has been advocated, and indeed, used with every success for water-resisting and high gloss lacquers. Ethyl cellulose is a cellulose ether made by the reaction of ethyl chloride upon alkali cellulose. It is a white, granular material freely soluble in a wide range of solvents. Like nitro-cotton, ethyl cellulose is available in low, medium and high viscosity grades. When comparing ethyl cellulose with collodion cotton, the viscosity of the former should be such that 69 pounds of ethyl cellulose in a given volume of solution produces the same solution viscosity as 100 pounds of nitro-cellulose in the same volume of solution. The advantages of ethyl cellulose over nitro-cellulose are first—gives more elastic and pliable films with less plasticiser (10% to 40% instead of 40% to 60%); less resin required to give a high gloss finish than is the case with nitro-cellulose; excellent resistance to light; good porosity, resistance to water and high breaking strength of film; better coverage than nitro-cellulose owing to the low density of ethyl cellulose. It is reckoned that it is 50% better in this

way than the nitro-cellulose and 25% better than cellulose acetate.

T. A. Kauppi and S. L. Bass (Amer. Paint J. 1937, 21. No. 28. 16) gives particulars of tests carried out with ethyl cellulose films which show that they have higher flexibility and toughness than either cellulose acetate and nitrate, but much lower hardness.

Apart from the use of ethyl cellulose in solvent solution for spraying, it may be incorporated in wax emulsions for wax finishes and increases coverage and improves the properties of the film.

Benzyl Cellulose

Benzyl cellulose is another promising cellulose compound which is finding a limited use in lacquers. It is not, however, so highly soluble as ethyl cellulose and does not give such clear solutions. One outstanding property of benzyl cellulose which is worthy of comment is its amazingly low moisture absorption figure, which is approximately four times as low as either nitro-cellulose or ethyl cellulose. Water permeability is also superior to either of the above. Breaking strength and general toughness of the evaporated film is less than nitro or ethyl cellulose and elasticity also inferior.

Besides nitro-cellulose, cellulose acetate, ethyl and benzyl cellulose, one or two other new cellulose compounds have recently received consideration. Cellulose acetobutyrate is an interesting new product which is soluble in a wide range of solvents, improved water resistance, dilution ratios and compatibility with plasticisers and lacquer resins. G. Schultze and R. Herbermehl (Farben-Chem., 1927, 8, 78–80) state that films of cellulose acetogutyrate show greater elasticity than cellulose acetate, so that smaller quantities of plasticiser

suffice. It can be mixed with nitro-cellulose in ordinary solvents.

As mentioned previously, lacquer films are all liable to become turbid or "blush" during the drying process. This "blushing" is due to one or several changes in the dope during drying, but more particularly to the presence of humidity in the atmosphere. Dr. Otto Jordan in his latest book, "The Technology of Solvents," says, "The absorption of sufficiently large quantities of water by the drying lacquer is most commonly brought about by the use of large proportions of low boiling solvents causing considerable reductions in temperature by their rapid evaporation, although here the atmospheric humidity has also to be considered. The trouble may most safely be overcome by the use of solvents giving use to very little evaporational cooling, and which are water repellent or form azeotropic mixtures with water of sufficient volatility. In the latter connection, butyl alcohol is again of service."

Cellulose Lacquers

In general works practice cellulose lacquers are obtained from manufacturers ready for diluting and spraying or brushing, and comparatively few tanners do any compounding themselves. The technique of nitro-cellulose spraying is very simple and consists in giving two or more coats; first the priming coat and then a final finishing one consisting mostly of pure lacquer containing little, if any, pigment or dyestuff.

Methods vary considerably according to requirements, and in some cases tanners give a priming coat and then send the goods (when thoroughly aired off) for a light staking so as to open out the grain. This is followed by a further coat of heavier pigmented dope and then a final spray of pure clear

lacquer. The finally finished leather, after the film has thoroughly dried, is often lightly stoned on the staking machine and then ironed with a hot iron or hot pressed on a machine.

Properly cellulosed leather can be grained, printed, hot pressed, rolled, etc., without suffering any detriment, but it is important to use always a lacquer specially adapted to the tanner's requirements. It may be that his processing requires a dope compounded to give maximum film tenacity and ten-

SPRAYING CELLULOSE LACQUER FINISH ON LEATHER . . .

sile strength, or maybe he needs a particularly elastic film. In all cases the tanner is recommended to take the cellulose finish manufacturer into his confidence and get him to adapt a finish for his own special needs. Of course, if he does not care to give away what he considers is vital trade information, he may wish to compound the dope himself, in which case the data given by the writer may prove of some value.

Finishing Water-Pigment Sprayed Leathers

In Europe considerable progress has been made in the lacquer finishing of water-pigment sprayed leather. The top cellulose dope gives a water-resisting finish and also improves the appearance. This method is a favorite for semi-chrome clothing leathers, and tanners point out that the casein bound water pigments give an excellent foundation film with high covering power and, of course, their cost is considerably less than the cellulose dope. There are, it should be pointed out, several snags in this processing and unless exactly the right technique is adopted there is a danger of the top film of nitrocellulose peeling off and so destroying the appearance of the leather.

Condition of Leather Is Important

The condition of the leather immediately previous to cellulosing is important. In the first place it must be free from moisture as the film will not adhere properly to the grain of damp leather. Then it must be free from any excess of grease, either saponifiable or unsaponifiable, as the presence of greasy patches always causes trouble.

The color must also be level if the leather is to be given only a cellulose finish. The latter has not the high covering power of a casein bound dope and in any case it is decidedly uneconomical to obtain uniform color effects with the expensive finish when the dyer should have seen after this.

Other factors contributing to success in cellulose finishing are: low humidity of the spraying booths and finishing department and the maintenance of normal temperature throughout the winter months. It is only just being realized that temperature conditions are important, and a normal fig-

ure of about 80° F. is recommended. The solvent must leave the film at a steady rate, otherwise complications are liable to arise in structure, which may cause it to be brittle, soft or lack good adhesive properties.

Success in nitro-cellulose spraying depends not only on using the correctly compounded dope of the right viscosity, but by insuring that the spraying equipment used is all in good condition.

The air should be filtered so as to keep the guns as clean as possible. Dirty compressed air inevitably leads to the clogging up of the gun and a considerable reduction of pressure, and this, of course, influences the so-called fan of the spray. The guns must also be free from cracks or leaks, which can also bring about a reduction of pressure. H. H. Glinke, "Industrial Finishing," August, 1938, gives some useful information about the testing of spray guns for leaks. He advises the operator "to fill the air hose with naphtha, then connect the hose to the gun and blow the air passage out. If there are any leaks, the naphtha can be seen spurting from the loose connections. This also helps to keep the gun clean. When guns are perfectly clean they shoot a good wide fan."

Types of Leather Finished with Cellulose

As regards the types of leather finished with cellulose, it may be said that there is no reason why all varieties of leather should not be sprayed or brush coated with the dope. It is, however, important to mention that the finish is relatively expensive and, therefore, unsuitable for skivers, cheap basils, etc., but is generally reserved for genuine morocco and full chrome clothing leathers, also to a certain extent for calf intended for shoe uppers.

The same finish is not suitable for all classes of leather.

One type, say gloving lambs, may require a very flexible finish, whereas calf for shoe work may need a finish of considerable body and moderately hard so as to resist abrasion. All these various factors have to be taken into careful consideration when dealing with nitro-cellulose finishes.

The factor which mainly influences success in nitro-cellulose finishing is uniformity of processing. First of all, the leather must be of uniform moisture content and fat content, then the color must be level (this is most important). The lacquer itself should not vary in consistency or composition and it upsets the whole procedure if the make of finish is changed, as it is sometimes purely because of a small price difference. It is easy to cut prices in the production of a lacquer by substituting low price hydrocarbon solvents for the necessary high boiling solvents, and although the viscosity may be the same and the finish appears in no way different from the one used previously, there is always a likelihood of trouble being encountered, such as blushing. It pays to give a good price for dope, and once satisfied, to adhere to one proved brand.

VII

SCIENTIFIC CONTROL OF TANNERY PROCESSES

SCIENTIFIC control of tannery processes is now regarded as a routine job for the works chemist who is expected to present reports on all new purchases of tanning materials and on finished leathers, as well as to undertake a long series of control tests on the various liquors used for processing. In his spare time he is expected to carry out a tricky, or at least somewhat spectacular piece of research so that he can add to the honor and glory of his employer by having a paper published under the exalted banner of a learned society. In England the works chemist, usually an enthusiastic but inexperienced young man fresh from college, has a bottle-washer assistant promoted from the general office who is taught to carry out titrations, do weighing and perform a good deal of the drudgery of the laboratory. This makes up the staff of that mysterious region known as the "lab."

WASTEFUL AND ILL PLANNED

In the writer's opinion, the present method of scientific control is extremely wasteful and ill planned. Instead of the laboratory being the real nerve-center of the tannery, it is merely a kind of machine designed to turn out an increasing number of tests, a good proportion of which are unnecessary.

This state of affairs is largely due to a desire on the part

of the works manager and the various departmental heads to shift responsibility on to the chemist. "Send a sample to the lab" has become a kind of catch phrase which, although convenient as a means of shelving decisions, is often quite meaningless because the results of difficult analysis are too often ignored or forgotten.

There is no sound reason why at least a portion of the routine tests carried out in the laboratory should not be distributed over the works and the various foremen or managers made to carry out certain necessary control tests for themselves. If a youth of fourteen without any previous scientific training can be relied upon to perform the Lowenthal titration, then surely the tanhouse foreman can be taught to do the same and moreover gain considerable knowledge and help from its repetition every day.

The chemist's real job is to act as liaison officer between the factory, that is the actual production side of the business, and the economic or sales side. He should make contact not only with the works manager but also the sales manager who is in a position to tell him about complaints from customers and their requirements. To undertake this special work the chemist must, however, be fully conversant with the complexities of manufacture and moreover have actual experience of what goes on behind the scenes.

The chemist who is far too busy to find time to spend in the works studying key processes is no great asset to the tanner. The latter, it must be remembered, earns no dividends from the large number of tests carried out in the laboratory; indeed, each test may cost him several dollars to carry out, but he stands a chance of making money, or at least saving some, when a skilled man is studying processes on his behalf with the idea of improving them or at least effecting economies.

Division of Control Work

Control work in the tannery can be safely divided into the following categories:

1. Observation by experienced operators.
2. Chemical analysis.
3. Practical tests.
4. Physical tests.
5. Microscopical examination.

The first is of the greatest importance and from the time the salted or fresh skins come into the tannery from the butcher or hide and skin market, the foreman and men should be encouraged to keep their eyes open and to enter any useful observations in a special report book, or on the space left for this purpose on the cards accompanying each order or pack of goods. It is surprising how even trivial details can be important when it comes to reviewing the reasons why a certain pack of goods is not up to standard. At every stage of processing men of experience should be able to draw conclusions and make useful notes as to the condition of the goods in their charge.

Chemical Analysis

Chemical analysis is usually ranked as the most important form of control and there is no disputing the fact that regular chemical tests do afford a great deal of valuable information. Where possible, however, use should be made of simplified tests which can be carried out by unscientific workers and the results easily interpreted. While the hydrogen electrode method of determining pH is undoubtedly the most accurate, it is only suitable for research where the time factor is not important. The glass electrode is now being preferred where extreme accuracy is not essential.

Naturally where expensive apparatus, such as the electrometric outfit for pH determination, is necessary, it is not advisable to leave it to the tender mercy of a works foreman, but there is no valid reason why he should not be taught to carry out simple colorimetric determinations of pH with a suitable comparator. This only gives rough estimations, but with careful use an accuracy of 0.01 to 0.02 pH is possible. F. C. Thompson, J. I. S. L. T. C., 17, 680, 1933, has found that colorimetric methods of pH control can be used with a reasonable degree of accuracy for testing soaks without sulphide; deliming liquors, tan liquors; neutralizing liquors from chrome tanning and water. It is fairly easy to explain to foremen the significance of the color changes and there should be no difficulty. The chemist's job is to teach the works staff to carry out a selected number of tests for themselves and to be able to record the results as well as interpret them in a practical manner. These tests must not be made too mysterious but kept as simple and intelligible as possible.

Worth of Analysis

One wonders whether it is worthwhile in some cases to undertake chemical analysis, especially of pancreatic enzyme bates. The usual casein and standard hide powder methods, although capable of producing useful comparative results in skilled hands, do not present the whole picture or enable the chemist to identify the various active components of the bate. As several chemists have pointed out, particularly A. K. Vlcek, Technicka Hlidka Kozeluzska (Gerbtechnische Rundschau, 84, 1935), the greatest error of analytical methods occurs in the preparation of bating material extract in that a portion of the enzyme is retained by the sawdust and is not determined. The author considers that purely empirical tests designed to indicate the relative activity of the

bates under test would in many cases give all the information necessary. Such tests would at least afford vital information regarding the freshness of the bate and the proportion of enzymes present. V. Kubelka, Coll. 1936, 34, has shown that when the activity of pancreatic enzymes is measured by the Kubelka-Wagner casein method, a diminution of activity 25 to 40%, is found if the bate is up to twelve months old.

Surveying processes in the light leather tannery, the author considers that the following could quite easily be controlled in the works itself without the chemist interfering. Deliming with the comparator; pickling by simple titration; tanning by comparator and Lowenthal titration; neutralizing chrome leather by comparator. This would leave the laboratory to carry out occasional analysis of lime liquors by the calcium hydroxide method (Atkins and Thompson), J. I. S. L. T. C., 1933, p. 568. Hide substance estimation (when essential) by the reliable method described by A. E. Best and D. G. Furzey, J. S. C. I., 1936, 55, 108T., which makes use of a mercury-selenium catalyst. Occasionally control of bates will be necessary, also gravimetric estimation of chromium and basicity of chrome tanning liquors, bath liquors, etc., fat content and analysis of finished leathers. On top of this the chemist must undertake analysis of samples, new materials in bulk, etc.

Physical Tests

It is only during the last few years that physical tests on a really comprehensive scale have been carried out in the tannery, and yet these tests are as important as any others and give more vital information than chemical analysis as to the quality of the leather. There are several dozens of physical tests and a score or more of apparatus or machines for carrying them out.

The most important from the light leather manufacturer's angle are the following: Bending; fold endurance; wear resistance; scuffability; tensile strength; resistance to sewing; waterproofness; stretch; permeability to air and water, etc.

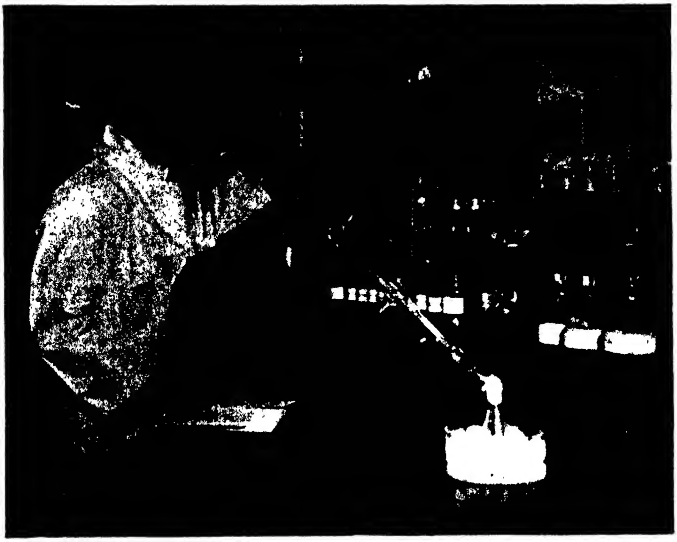
The shrinkage of leather can now be accurately determined by means of an ingenious but quite simple machine invented by W. J. Chater, J. I. S. L. T. C., 432, 1938. The instrument allows a series of shrinkage tests to be carried out rapidly and easily so that there is no necessity to watch the experiments continuously. With this apparatus a series of tests to ascertain whether a desired condition of pelt or tanned product has been attained may be carried out with ease, an inspection of the graphs showing the progress being made towards the condition aimed at.

At least half a dozen physical tests should be periodically carried out on certain types of leather, particularly upper and clothing leathers. These tests afford data, which in association with the findings from chemical tests will give a true indication as to the real quality of the leather and how it will stand up to wear. The U. S. Bureau of Standards has done a great deal of work on the destructive action of various agencies and its published results are well worth studying.

Microscopical Examination

The importance of microscopical examination is not always allowed by chemists, many of whom are unacquainted with the first principles of microscopy. Yet the microscope can help to complete other scientific examination and it is particularly useful in diagnosing the cause of stains, cracked grain, spue, moulds, etc. As regards stains, a method put forward by G. M. Sleichter, J.A.L.C.A., 478, 1938, should

prove very helpful. This method enables the chemist to see the relative amount of inorganic salts in a section of skin, hide or leather and also to determine by visual examination the position of these deposits. Cut sections, 25 microns or less in thickness are prepared, dehydrated with the alcohols



SCENE IN A TYPICAL TANNERY LABORATORY SHOWING CHEMIST CARRYING OUT SIMPLE DISTILLATION OF A NEW CELLULOSE FINISH SUBMITTED FOR ANALYSIS. . . .

then mounted on pyrex slides with a film of glycerine-gelatin jelly and then thoroughly dried at 60° C. on a hotplate. Incineration is best done at 650° C. using an electric furnace. Thirty to forty minutes is allowed for incineration and this is followed by cooling for 2 hours. The slides are then immediately protected by a clean cover-slip and examined with a low power.

Micro-chemical tests can also play an important part in

control work and once the technique has been mastered various qualitative tests can be carried out with speed and efficiency. N. Jambor and Z. Demeny, Coll. 1936, 74, give some useful methods for the leather chemist.

To achieve success in the laboratory the chemist must be able to co-ordinate the various branches of control under his supervision, and to translate results so that they can easily be understood by executives and works foremen. Where possible, results of practical tests with a new tanning material, finish or fat liquor should accompany laboratory findings. The wisdom of conducting small scale works experiments is now being fully appreciated by a number of large firms in England.

A Review of Recent Important Patents

A review of progress made in the light leather tannery as shown by recent patents is very instructive and clearly reveals the tendencies in modern methods of production.

Patent literature is rather voluminous concerning the application of enzyme preparations both for depilation and bating. An interesting patent by *O. Rohm,* B. P. 495,408, describes a process of treating hides and skins for unhairing with fungi tryptases from various types of Aspergillus. Before or after enzyme action the goods are subjected to the action of oxidizing agents and sulphur-containing reducing agents. Suitable oxidizing agents are alkali nitrates and nitrites, hydrogen peroxide, sodium peroxide, sodium perborate.

Enzymes have also been proposed for soaking back obstinate dry hides and skins. *Pancreol, Ltd.*, B. P. 474,991, suggest a dilute solution (up to 0.25%) of papain or bromelin. Activating and other salts may be added to the bath, e.g., ammonium chloride, sulphate, sodium sulphide and also ani-

mal enzymes and inert powders or fillers. The goods are tumbled in the solution for an hour or two and if of specially resistant type may then be broken on the beam and returned to the liquor for further treatment.

For the bating of hides and skins the use of an alkali metal polyphosphate or metaphosphate in conjunction with a suitable enzyme is recommended by *A. H. Stevens (Hall Laboratories, Inc.)* B. P. 471,753. The optimum pH of the solution is stated to be 7.4.

New enzymes for bating include proteases from fig, banana or mulberry. *Pancreol, Ltd.,* in their patent B. P. 475,660, state that hides and skins from which the epidermal layer has been removed by an unhairing process may be bated by means of an alkaline solution containing a vegetable protease of the type of papain or bromelin after or in conjunction with a tryptic enzyme in much higher concentration. Deliming salts and activators and inert fillers may be present in the bath.

The largest number of patents have been taken out to cover new tanning processes, particularly sulphonated condensation products of cheap coal tar products. The *I. G. Farbenindustrie Akt-Ges* have been well to the fore in developing new synthetic tannins, some of which make use of sulphite cellulose lye as a raw material which can be linked up with suitable phenolic or other groups. For instance, B. P. 496,898 covers a process of manufacturing tanning agents by treating ligninsulphonic acid compound, e.g., sulphite cellulose lye with a condensation product derived from an aromatic hydroxyl compound and an agent capable of linking aromatic nuclei. In the examples quoted, sulphite cellulose lye which has been heated with caustic soda solution is heated with aqueous ammonia and mixed with a resin prepared from phenol and chloracetone; in another example quoted, sulphite cellulose lye is mixed with a resin made by

treating crude cresol and formaldehyde with caustic soda and then acidifying with sulphuric acid. The use of sulphite cellulose lye for the preparation of synthetic tannins is significant because it means that the lye is now considered to be more suitable for manufacturing cheap synthetics than as a preparatory tanning agent. This fact has, of course, been realized for some years by tanners who have had experience of waste lyes and found them to be of very doubtful practical or economic value.

As a result of the grave shortage of pure tanning extracts and other raw materials in the totalitarian states, concerted efforts are now being made to develop substitutes. As a direct result of the policy of self-sufficiency a considerable amount of interest is now being shown in iron tannages. The German chemists have attempted to produce large molecule iron compounds of a highly complex nature which would be unlikely to break down easily within the actual fibrils of the skin. Although it is unlikely that iron tannage will ever take the place of chrome owing to the comparative lack of stability of both ferrous and ferric solutions and the permanence of chrome tannages, it is a fact that when the Fe group forms part of the central structure of a new large molecule, there is a far better chance of the leather being permanent.

B. P. 470,530 describes a method of producing a number of iron compounds for tanning purpose. Hexaurea iron chloride formed by adding the calculated amount of urea to iron chloride is named and also compounds or iron with formamide, acetamide, condensation products or aldehydes with amines or ammonia, etc. Other methods proposed consist of tanning hides or skins in a bath containing iron chloride and acetamide and afterwards treating the goods with naphthalene sulphonic acid-formaldehyde tanning agent. The author considers that these new methods offer great

promise, as it is obvious that the most durable results obtained with iron compounds will be with similar kind of groupings to the highly complex natural tannins, and it is suggested that iron tannage should be followed by treatment of the goods with suitable synthetic materials of the Neradol type.

The tendency to make use of a large tanning molecule is clearly obvious in the patent literature covering the synthetic field. The introduction of colloidal silicic or stannic acid to the already complex sulphonic acid condensation product type is proposed by *Geigy Akt-Ges,* B. P. 465,674. The silicic or stannic acid may be introduced during the manufacture of a synthetic tanning agent by adding an alkali silicate or stannate to neutralize an acid solution of the tanning agent. In an example given, a mixture of naphthalene sulphonic acid, dioxydiphenol sulphone, formaldehyde and water is heated to boiling and neutralized with water glass and caustic soda. Another example gives cresol sulphonic acid, formaldehyde and water is warmed and then neutralized with water glass and caustic soda.

The use of phosphates as tanning agents and also for pre-dyeing applications, etc., has been put forward by a number of people. For instance, *A. H. Stevens (Hall Laboratories, Inc.),* B. P. 472,164, proposes the use of a solution of an alkali-metal polyphosphate for treating chrome leather prior to dyeing. The goods are washed and processed in a solution of 10 pounds of sodium metaphosphate in 50 gallons of water.

As regards tanning with phosphates, a representative patent is B. P. 478,443, taken out by *Chemische Fabrik J. A. Benckiser Ges.* This states that hides and skins can be tanned by treating with polymeric metaphosphoric acids or their water soluble salts with uni or polyvalent metals, ammonia or organic bases, either alone or together with other

mineral or vegetable tanning agents, the pH values of the solutions being adjusted to not more than 5.5. In an example, kid skins are tanned with a solution of iron ammonium alum and sodium hexametaphosphate and also with a solution of potassium chrome alum and sodium hexametaphosphate.

In a later patent, B. P. 484,781, *Chemische Fabrik J. A. Benckiser Ges.*, covers the tannage of hides and skins with polyphosphoric acids or their salts with metals, ammonia or organic basis, together with water soluble silicates which are applied separately or simultaneously. According to an example a sodium polyphosphate is employed in conjunction with water glass, the pH of the solution being gradually brought to 2.5 by addition of acid.

The theory of metaphosphate tanning has been explained by *C. Reiss, Stiasny Festschrift*, 1,937,366, who states that the tanning action is an intermediate stage between the purely preparatory pickling and a true tanning. It appears to consist of a salt formation at the basic groups of the collagen. The quantity of irreversibly bound $(HPO_3)_x$ is apparently equal to the acid combining capacity of the collagen and collagen tanned with metaphosphoric acid is practically unable to combine with any more acid. The tanning action of metaphosphoric acid is explained by a tying up of the principal valency chains of the proteins, following the multiple salt formation of the polymerised metaphosphoric acid with the basic protein groups. This, it is stated, accounts for the absence of swelling in acids and also the increase in shrinkage temperature.

The writer is of the opinion that the future of metaphosphate tanning lies in the combination of the phosphates with other mineral or organic tanning agents. There is no real commercial value in a straight phosphate leather except perhaps where there is a definite need for a leather highly resist-

ant to heat. The use of metaphosphate in conjunction with the condensation products of urea and formaldehyde is recommended by the author as well worthy of consideration by tanners.

Incidentally, sodium phosphate has been proposed for fireproofing leather and *M. C. Lamb*, B. P. 465,533, describes a method whereby vegetable tanned leather, which has been freed from grease or oil, is treated with a soluble aluminum salt and then with a chemical substance, which will form an insoluble aluminum compound in the pores of the leather. According to an example, leather is first drummed with aluminum sulphate and then with the addition of sodium phosphate.

Several interesting methods have been proposed for using formaldehyde and one or two are well worth mentioning. *Rohm and Haas Akt-Ges*, B. P. 483,598, combine formaldehyde with complex compounds of aluminum salts and oxalic acid or its salts. According to an example, hides are fulled in a solution of oxalic acid, aluminum sulphate, sodium chloride or alkali sulphate and formaldehyde, and after some hours a solution of sodium carbonate is added. The hides or skins are finally washed and greased with sulphonated oil. Hides which are formaldehyde tanned as described may be further tanned according to examples given by treating with sodium silicate and formic acid, iron sulphate chloride and sodium silicate, etc.

Another method of formaldehyde tannage which is claimed to take only one hour makes use of a solution of formaldehyde and alcohol. B. P. 482,266, taken out by *G. F. Lloyd*, describes the process which consists of treating the goods with a solution containing formaldehyde and alcohol and then with an alkaline solution to close the pores of the skin and retain the tanning agent therein, the whole process occupying less than one hour.

A revolutionary method of quick tannage was taken out by *Tanning Process Co.* in 1937 and is described in B. P. 493,850. After treatment with tanning material and before completion of the tanning action (preferably before complete penetration of the tanning liquid) the goods are subjected to heat treatment by a gaseous medium, e.g., air at 200° F., or over, so as to remove liquid from the work and complete the tanning. In applying the method in chrome tanning, the skins are first subjected to a chrome bath which produces little or no tanning and then with a reducing solution, the skins being slicked out on boards after or before the second treatment. The slicked-out skins are then subjected to the heat treatment and afterwards washed, fat-liquored, colored, dried, etc.

Fat-liquoring, Etc.

Recent experiments and patents suggest that quaternary ammonium salts are likely to prove of importance to the tanner as useful additives to the dye bath, especially in the case of chrome leather where acid or substantive dyestuffs are used. It is claimed by *I. G. Farbenindustrie Akt-Ges,* B. P. 485,254, that chrome tanned leather treated with quaternary ammonium compounds dye more evenly due to the fact that there is no formation of difficulty soluble compounds which are often responsible for exaggerating grain defects.

E. I. Du Pont de Nemours & Co., B. P. 477,981, prepare quaternary ammonium compounds for tannery purposes from a tertiary amine and a halogenated compound or by alkylation, cycloalkylation, arylation or aralkylation of an amine, the components in either case being so selected that the products contain at least one group of more than five carbon atoms. It is stated that the products are useful in

tanning, especially fat-liquoring. They may be used as such or in admixture with one another or with soap or other saponaceous substances.

The value of phosphatides, especially lecithin for addition to fat-liquoring emulsions, is well known now but the difficulty is to obtain really stable emulsions. B. P. 464,100, taken out by *B. Rewald,* describes a method of preparing stable compositions by treating phosphatide with a water soluble hydroxy aliphatic acid such as lactic acid. For example, a stable product may be obtained from a mixture of 65% commercial phosphatide (containing 30% oil) and 35% water, to which is added 20% concentrated lactic acid solution. A mixture of 5 parts soya bean phosphatide, 50 parts of water and 5 parts of lactic acid is stable and may be diluted with 100 parts of water.

VIII

WASTE PRODUCTS OF THE TANNERY

THE most valuable byproduct of the tannery is hide and skin offal, which is usually in demand by the glue and gelatine manufacturer. Next in value is recovered fat from frizings and fleshings. Then blue chrome shavings which, when suitably treated to remove the chrome salts, can be boiled down to make a medium quality glue. Following in importance comes wool waste and goat's hair, also calf hair if the market is good.

Leather waste, apart from blue chrome leather and alum leather scraps, is very seldom in demand in normal times, but in the dictatorship countries and during wartime scrap of all kinds is needed for making up into various substitutes. Although there are almost hundreds of methods of utilizing leather scrap the amount which can successfully be incorporated in any aggregate is small as the presence of more than about 10 per cent scrap tends to weaken the strength of the mixture. It is, however, of interest to consider a few methods of utilizing leather scrap for making substitutes and new plastic compounds.

As regards the possibility of making fertilizer out of scrap, this is very remote, and, indeed, the only successful method, which is not, however, economical, is to dry distil the leather and recover the ammonia as ammonium sulphate. Spent tan is a drug on the market and apart from a few uses,

such as a dressing for riding tracks, circuses, etc., it is practically useless. Some tanners used to dry the spent tan and burn it in their furnaces, but today very few utilize it in this way as it is a poor fuel and is bulky and difficult to handle economically.

Hide and Skin Pieces

The best quality glue and gelatine is made from calf pieces and it is generally the practice of the tanner to keep calf offal separate from the other kinds. The majority of tanners keep the "roundings" and "pates" piled in heaps covered with sacking which has been dampened with lime liquor. Fleshings, which are inferior for glue making, are generally preserved in a weak solution of lime in large tubs or pits. Calf feet do not yield a large quantity of glue, but they are of special importance as they are rich in neatsfoot oil which can be recovered fairly easily. Waste from sheepskins forms the largest portion of the glue manufacturer's stock. It is usual to keep the roundings or trimmings separate from the fleshing.

Methods differ slightly of preserving the offal, but the writer considers that it is preferable to keep them in shallow concrete pits containing a small quantity of lime liquor and to cover them over with sacking moistened with lime liquor. The offal should not be allowed to remain untouched for longer than a few days, and it is a good practice to get them turned over with a fork every day, or even twice a day in hot weather. This method of preservation is preferable to the total immersion of the pieces in a pit containing lime liquor. If this method is used there is always a danger that intensive hydrolysis will take place and the stock go "mealy" and lose its glue-making qualities. It is important to preserve the collagen and other proteins in their natural condi-

tion and not to break them down into simpler bodies which have poor glue-making properties.

The following stock classifications are generally accepted:

Calf (roundings and pates)
Calf (fleshings)
Hide (fresh and limed) } Pieces and fleshings
Hide (dry salted) } Pieces and fleshings
Hide (flint dried) } Pieces and fleshings
Sheep (roundings and pates)
Sheep (fleshings)
Goat pieces
Goat (fleshings)

Recovery of Fat from Fleshings

There are two sources of fat which the tanner can use. First of all, frizings or shavings obtained in the beam-house when sheepskin linings are being prepared for oiling and chamoising are the most profitable source of fat. Next follows the ordinary fleshings removed by the machine in the normal way. The best method of treating both fleshings and frizings is to soak them in boiling water for a few minutes preparatory to pressing in a hydraulic press. The thick creamy liquid which exudes from the plates of the press can be collected and boiled with live steam in coppers so as to separate the fat from the lime liquor. The aqueous layer is run off and the fat boiled up with live steam in the presence of dilute sulphuric acid for several hours. It is then allowed to cool, the aqueous layer again run off and the fat washed with several changes of warm water until free from acid.

Fat recovered in this way is usually white and of a buttery consistency. It sells readily to soap and margarine manufacturers. The residue left in the hydraulic press is useful as a fertilizer, but is of no use for glue making.

Goat's Hair (Calf and Cow Hair)

This is the only hair really worth recovering at the present time, but it may be that calf and cow hair finds a market in certain districts. In any case, the same method of preparation applies. After depilation and rubbing, the hair is roughly graded. The white and light colors are separated from the black and dark colors. Each grade is then washed separately in a large galvanized iron tank by simply moving it about with a large fork so as to open out the clots and remove as much free lime and dirt as possible. Several washings may be necessary to clean the hair. This method of preparation is rather primitive and where there is a steady demand for the hair it pays the tanner to install a hair washing machine. In small tanneries, however, the simpler the method the better. After washing, the hair should be hydro-extracted or drained on wire gauze frames. Afterwards it must be dried on frames in a hot stove and finally baled ready for market. Generally speaking it does not pay the tanner to go to very much trouble to clean the hair owing to the heavy cost of labor involved and the very small price obtained for the hair.

Waste Wool

Even when fellmongering is done outside the tannery proper, a certain amount of wool inevitably accumulates and is worth preparing for market. The procedure recommended is to wash it in a tank, using several changes of water, and then to hydro-extract and dry on wire gauze frames in a hot stove. When a hundredweight or so of wool has collected it should be rewashed in warm soapy water, rinsed thoroughly, hydro-extracted and finally dried. The extra trouble

involved in cleaning the wool is well worth while if the market is at all favorable, otherwise it will not pay the tanner. A point worth remembering is that the tanner will be well advised to store his odd scraps of wool until sufficient bulk is obtained to command a fair price. It is distinctly uneconomical to sell in small lots.

Recovery of Fat from Scrap Leather

In certain circumstances it may be profitable to remove the fat from leather and to refine it so that it is suitable for soap making. The best method is to soak the scrap in one of the chlorinated solvents and then to distill off the free solvent and so recover the fat. The latter is usually dark and possesses a strong and disagreeable odor. Various methods of refining are available and while some require a special plant, others are relatively simple to carry out. An excellent method is described in Seifensieder-Ztg. 65, 1024–5 (1938). The fat is saponified with the calculated amount of caustic lye, noticeable amounts of volatile odorous materials are separated. During the salting out process dirt and dark colored ingredients separate in the lye liquor. If this procedure is carried out a number of times, in most cases the fat so treated will be much improved in color and in odor. If desired, the fat may be treated with bleaching earth and filtered.

Leather Scrap for Substitutes

Both vegetable and chrome tanned leather scrap finds a number of interesting uses, particularly for the manufacture of artificial and so-called regenerated leather. A recent patent (B. P. 491,197) protects a method of utilizing scrap in this way. The disintegrated leather scrap or cuttings and

dispersions of rubber is treated with glycerol, rubber latex, aqueous dispersions of metallic oxide such as titanium dioxide, or dye solutions, by contacting it with the surface of a roller coated with the liquid, as by being partially immersed in a liquid bath. The roller may be rotated against the direction of movement of the sheet, a doctor blade being employed to scrape off excess of liquid. Several treatments may follow in succession. The liquids may contain a wetting agent; for instance, the salt of a sulphonated alcohol. The sheet may be partially dried before treatment.

A process recently patented in America and assigned to National Products Corp., Washington, D. C., appears to have very interesting possibilities. The process is relatively simple and consists of soaking the scrap in an 8 per cent solution of sodium carbonate for about 10 hours. The mass is then placed in a steam-jacketed kettle, where it is subjected to a temperature of 190° F. for further softening. Acetic acid is added and the material is stirred and heated for another hour, by which time the scrap leather is reduced to a heavy viscous fluid. The liquid is then stirred while trienthanolamine is added as a plasticiser. After cooling to 90° F., formaldehyde is added, which renders the solution in the dried state waterproof. It is claimed that the solution can be extruded into sheets and is similar to transparent cellulose film.

There is no doubt that plastic materials could be produced from leather but it is too early in the day to say whether they would be able to compete with the many synthetic products now on the market. A process which may one day have a commercial significance is suggested by the author. The leather scrap is digested with sodium carbonate or caustic soda under pressure and the liquid neutralized, filtered and treated with sebacic acid under pressure. The resulting plastic mass is worth investigating.

An interesting use for leather scrap is mentioned in a fairly recent British patent (487,518). The wall structure of porous pots, etc., for seedlings is composed mainly of felted leather scrap, e.g., sheeted on a paper making machine into a board. The leather may be disintegrated dry or wet by impact or other machines. By adding lime, etc., the acid in the leather may be neutralized after the pot has been imbedded in the soil. Wool, hair, mineral wool or asbestos may be added in relatively small quantities. Insoluble or soluble fertilizers such as ammonium sulphate and sodium nitrate may be added to the disintegrated leather or applied in aqueous solution to the finished pots.

Leather scrap is used to a limited extent in the manufacture of special composition washers and gaskets. It is said the inclusion of small quantities of leather waste, about 10 per cent, helps to preserve the rubber and therefore serves a most useful purpose.

Leather Scrap as a Fertilizer

It should be remembered that ground, roasted or steamed vegetable tanned leather ranks as one of the least active of all nitrogenous fertilizers. It contains when dry only 5–10 per cent nitrogen and this is so firmly combined to the tannin groups that no satisfactory decomposition in the soil takes place. Therefore, before leather waste can be used for any useful purpose as a manure it must be treated in such a way as to render the nitrogen available to the vegetation.

There have been a number of patents taken out to cover the manufacture of leather fertilizers, but nearly all of them embody the same fundamental idea, namely, the digestion of the leather with sulphuric acid and the subsequent treatment of the mixture with phosphates. In the writer's opinion it is not economical or worthwhile to treat leather so as to

make a fertilizer, and in any case the less leather in the mixture and the more phosphates, the more valuable will be the product.

The production of ammonium sulphate from leather is, of course, possible, but in normal circumstances it is not economical. The Committee of the British Association in 1917 obtained 23–25 per cent of crude ammonium sulphate by the dry distillation of condemned army boots and absorption of the products by sulphuric acid. Dr. L. Bonavia, however, was only able to obtain 13.26 per cent of neutral sulphate of ammonia by distillation. On dissolving the leather in sulphuric acid, however, and converting the nitrogen into ammonia, corresponding to 35.2 per cent neutral sulphate, was obtained.

Professor Arturo Bruttini in his "Uses of Waste Materials" gives the following information concerning army boots: "Worn out army boots have been chiefly used to obtain 'leather gas,' which resembles Dawson gas or poor gas. This was done during the years 1919 to 1920 at Modena, utilizing the large quantities of boots that had accumulated at Saliceta S. Giuliano. An ordinary town gas generator is used with injection of water and compressed air under the furnace. The calorific power of the gas comes out at about 1,300 calories."

Spent Tan

The amount of spent tan obtained in the ordinary light leather tannery using large quantities of extracts must necessarily be very small; the bulk of the spent tan is sumach. This has practically no value at all and cannot even be dried and used for steam-raising. The author believes that on the Continent a certain amount of spent sumach and other tans is used in the manufacture of briquettes, but these have a

poor fuel value and could never sell in England or America in normal times.

The author considers that it might be commercially possible to treat some spent tans, such as hemlock and myrobalans, which are high in lignine and natural resins, with formaldehyde and convert them into resins which could be used for softening water or even the purification of sewage. It will be remembered that tannin resins have base exchange properties and interesting potentialities for water softening and there is no reason why resins made from the spent tans should not also find some use for the same purpose.

IX

HEALTH HAZARDS IN THE TANNERY

A Study of Dangerous Gases and Vapors

Although the danger to health arising from exposure to toxic gases and vapors and the handling of dangerous liquids is not as acute in tanning as in many other industries, it is a fact that the respective hazards should be very clearly recognized.

One of the commonest gases found in the tannery is hydrogen sulphide. This gas is found in empty pits which once contained sodium sulphide and lime, also empty tan pits used for heavy leather and, of course, in the sewers which convey effluent to the river, canal or drainage system. Traces of hydrogen sulphide are also found in the atmosphere of the limeyard and in the puering or bating shop, especially when natural dung is used, and also the drenching shop. It may be said, as a kind of rough ruling, that this gas is present wherever there is a decayed protein matter containing sulphides or sulphur.

Hydrogen sulphide is a highly toxic gas and in concentrations of 1 in 1,000 by volume or higher, is nearly as toxic as hydrogen cyanide and may act with equal rapidity by a paralyzing of the respirator center of the brain. According to the table prepared by the British Department of Scientific and Industrial Research: 1 in 2,000 parts by volume is very dangerous if inhaled for 15 to 30 minutes. It causes severe

irritation of the eyes and respiratory tract with risk of pneumonia or serious injury to the lungs, which may readily prove fatal; 1 in 5,000 is dangerous if inhaled for one hour, and causes severe irritation of the eyes and respiratory tract. Eyes are affected after 6 to 8 minutes; 1 in 10,000 causes symptoms of local irritation of eyes and respiratory tract after one hour's exposure.

The writer has never found the gas in such concentrations as specified above, but over a number of years he has noticed that workers in the puer shop of a well known tannery were always in failing health and suffered a great deal from respiratory diseases, such as bronchitis. The concentration of gas varied quite considerably according to the extent of use of natural dog dung, which was used in conjunction with artificial bates. Average concentration about 1 in 50,000, which, although small, was sufficient to cause or promote insidious deterioration of health over a period of years.

Various methods are available for detecting and estimating hydrogen sulphide in the atmosphere of the tannery. The method recommended and standardized by the Home Office authorities in Britain is the lead acetate test which is easily adaptable to a quantitative basis. The method is carried out by drawing a known volume of the suspected atmosphere through the test paper. The stains are then compared with artificial standards. This test will detect concentrations of hydrogen sulphide as low as 1 part in 150,000 parts of air by volume. It is pointed out by the Government authorities who have evolved this standard test that concentrations lower than 1 part per 30,000 are not harmless, but may be regarded as unlikely to cause serious effects if the exposure is not continuous or prolonged.

The official recommendation made for the treatment of serious accidents through gassing by hydrogen sulphide consists of removing the patient out of the contaminated atmos-

phere into the fresh air and wrapping him in a blanket. Artificial respiration with oxygen should be started at once and continued even after it may seem to have failed.

Sulphur Dioxide

In the bleaching of chamois leather this gas is quite frequently used and is made by burning flowers of sulphur in iron pots placed at intervals on the floor and under the damp leathers which are suspended from racks. Although the room is hermetically sealed immediately after the sulphur has been ignited, there is a danger of gassing when the doors are opened and the goods removed. The room is not always adequately ventilated and pockets of the gas are liable to collect in corners of the room. Knowledge of the toxic properties of the gas, detection and the best method of treating cases is, therefore, of importance.

In high concentration sulphur dioxide is irrespirable and causes asphyxiation. In lower concentrations it is irritating to the eyes, nose, throat and lungs and may cause inflammation of the nose and throat and set up bronchitis. According to Henderson & Haggard (Noxious Gases, 1927), 1 in 100,000 is the maximum concentration allowable for several hours' exposure and 1 in 2,000 is a concentration shown to be dangerous for even short exposures.

A simple test, making use of the starch-potassium iodate-potassium iodide-glycerol test paper, has been adopted as the standard method in Britain for estimating traces of sulphur dioxide in the atmosphere. This test is readily capable of detecting a concentration of 1 part in 100,000 and, in certain circumstances, 1 part in 250,000.

In the case of an accident due to gassing by sulphur dioxide, the patient should be removed into the fresh air and wrapped in a blanket to keep him warm. Send for a doctor.

If breathing is weak, or has stopped, artificial respiration with administration of oxygen should be started at once and continued for hours, even after it may seem to have failed.

Benzene Vapor

Although benzene is not used to any great extent in the leather industry, it finds some application for degreasing purposes and is also used in glue works for degreasing bones and other stock.

In high concentrations benzene acts as a narcotic and in low concentrations it affects the blood and blood-forming organs of the body. It is pointed out by competent medical authorities that susceptibility to the poison varies considerable, but women and children are quickly affected.

The figures given by Henderson & Haggard (Noxious Gases, 1927) for dangerous concentrations of benzene vapor in the atmosphere, are as follows:

1 in 700 to 1 in 300: Slight symptoms after several hours' exposure.

1 in 300 to 1 in 200: Maximum concentration that can be inhaled for 1 hour without serious disturbance.

1 in 140: Serious illness with 30 minutes' to 60 minutes' exposure.

1 in 50: Rapidly fatal.

It is pointed out that poisoning may occur in atmospheres where the vapor ranges in concentration from 1 in 200 to 1 in 5,000. Owing to its low solubility in the blood, most of the benzene absorbed is eliminated through the kidneys—a slow elimination which favors cumulative effect on repeated exposure.

The standard routine tests for benzene vapor in industry recommended by the British authorities involves the absorption of the vapor in concentrated sulphuric acid containing a

trace of formaldehyde; an orange-brown color is produced, even if only slight traces of benzene are present.

In case of poisoning, the best advice is to remove the patient into the fresh air, wrapped in a blanket to keep warm. Send for a doctor. If breathing is weak or has stopped, artificial respiration with administration of oxygen and carbon dioxide should be started at once.

Benzine and Petroleum Spirit

Petroleum spirit in one form or another is used to a considerable extent in modern degreasing plants in tanneries and needs to be handled with considerable care, not only because it is so inflammable, but because it has toxic properties which are not always fully appreciated.

The U. S. Bureau of Mines (1921) and Lehmann (1912) have estimated the concentrations of benzine vapor producing slight or severe acute symptoms: Perceptible odor, 300 parts per million; dangerous by inhalation for short periods, 11,000–22,000 parts per million; rapidly fatal, 24,000–30,000 parts per million.

Lehmann has worked out concentrations in mg. per litre of air respectively: Fatal immediately or later, after ½–1 hr., 30–40 mg. per litre; dangerous to life, after ½–1 hr., 25–30 mg. per litre; tolerated for ½–1 hr. without immediate or late effect, 10–25 mg. per litre; toxic effects after several hours' inhalation, 5–10 mg. per litre; tolerated for 6 hrs. without symptoms, 10 mg. per litre.

It is amazing, the ignorance that exists regarding the toxicity of petroleum spirit, which, incidentally, varies a good deal in toxicity according to the grade or fraction of spirit present. The writer once knew the foreman of a degreasing plant who bathed his eyes in benzole so as to make them stronger. Although it was pointed out to him

what a stupid practice this was, he took no notice and continued with the fantastic treatment, with the result that he eventually went blind.

The effect of benzine, benzole and other petroleum spirits on the body is very complex, but they do act as a narcotic and have a preliminary irritating effect on the brain. Chronic benzine poisoning invariably causes anaemia and the symptoms are said to be giddiness, black spots before the eyes, insomnia, headache, somnolence, asthma and gastro-intestinal disturbance.

Toxic Vapors from Cellulose Lacquers

These may consist of several, the persistence and concentration of any one depending on the temperature, as both low and high boiling point solvents are present. Petroleum solvents are always likely to be present and so also are amyl methyl and ethyl acetate, acetone, ethyl alcohol, Cellosolve, etc.

All these solvents and, in fact, all other solvents and plasticisers, etc., are toxic and differ only in degree of toxicity. Naturally the lower the volatility of the solvent, the safer it is to use, but in spraying lacquers it is necessary to point out that very high concentrations of vapor may be present due to poor ventilation and lack of sufficient draught of air to draw away the vapor.

The toxic effects of the various volatile constituents of modern lacquers vary considerably; thus, in the case of amyl acetate, a fairly common trouble is conjunctivitis and various nervous symptoms and in others the vapor has definite narcotic and irritation effects and, in chronic cases of poisoning, produces or promotes gastric disturbances.

The main difficulty in considering the toxicity of the many solvents used in the preparation of lacquers is that their un-

suspected and insidious long-range effect is always liable to be overlooked. Several of the later members of the glycol group, for instance, give no immediate warning by unpleasant effects on inhalation, but cause serious physiological changes after a period of time, which, however, varies a good deal in length. The wise precaution in all cases is to consider solvents as highly toxic and not to accept the glib assurances of manufacturers' salesmen that their products are really safe. Real safety is only assured by avoiding inhalation. To ensure this means that well planned and adequate ventilation must be installed.

X

SOME PRACTICAL PROBLEMS IN LIGHT LEATHER MANUFACTURE

It is no exaggeration to state that the tanner experiences more problems in his day to day work than any other manufacturer. This is due to several reasons, the most important being the peculiar and, as yet, little understood nature of the protein raw material and the lack of complete control and real scientific knowledge of manufacturing processes. Difficulties which crop up in the tannery call for immediate solution and there is usually a very small margin of time allowed during which measures may be taken. This is particularly the case during those early key processes, such as liming, bating and pickling.

A fairly recent example of a problem which needed a quick answer is the following. At a works specializing in vegetable tanned roans for hat bands or linings it was noticed that a varying percentage of goods were flake marked during tannage, which was carried out in a drum. A careful study of the process showed that flaking might be due to several factors. First of all it could be caused by the skins knotting in the drum. Then flaking would result if the green goods were run in too strong a liquor or allowed to remain stationary in moderately strong liquor before the tan had struck. The composition of the tan liquor at the commencement of tanning also influences flaking. For instance, while sumach is what might be called "kind" to green goods, that

is, unlikely to cause flaking, highly astringent tannins, such as quebracho extract, are rather prone to cause trouble.

To check up on all these possibilities took a few days, at the end of which time it was found that knotting of the goods did not take place and that the strength and composition of the first liquors were exactly the same as usual. It was, however, revealed that sometimes the green goods were loaded into the drum much later in the day than was customary and this caused one or two headaches on the part of the staff, which had to determine whether this factor contributed to the trouble in question.

After consultation with the works manager it was decided to keep careful watch on a pack which was passed into the tan drums at 2:30 p. m. instead of 9 a. m., and allowed to remain in the liquor all night, as was the usual custom. When the pack was examined next morning, it was found that 15 per cent were badly flaked, 10 per cent moderately flaked, and 5 per cent just marked. By making it a firm rule that all green goods from the drench and pickle should enter the tan drums not later than 9 a. m., the trouble was cleared up, and to make it less likely that flaking would result even if the goods were delayed, the percentage of sulphite quebracho in the early liquors was cut down by half and replaced by myrobalans.

The solution of this rather tricky problem, which took up the best part of a week, was only possible by the staff working as a team. The tannery foreman obviously provided the vital facts, but the warehouseman who examined the crust goods and the works manager who collated the information all helped considerably to analyze the trouble and then to synthesize it.

In the writer's opinion, it is only by team work and the occasional assistance of specialists that it is possible to find

the answer to works problems. Very often they arise solely through carelessness.

For instance, some years ago the writer came across a tanner handling market calfskins for willow uppers who experienced occasional trouble in the limeyard through the burning and damage of goods. The foreman was questioned but could offer no proper explanation. A careful and unsuspected watch was kept on the work and it was eventually discovered that when there was a rush of goods from the unhairing machines and a demand for new limes, the lime liquor was made up by allowing the quicklime to slake only for an hour or so before running in the desired amount of water and making up the pit ready for the depilated skins. The burning or, rather, scalding of the skins was due to one simple cause, namely, the heat generated at the bottom of the pit by unslaked lumps of lime. Naturally, only those skins directly in contact with the lime were affected.

To avoid any repetition of this trouble, use was made of hydrated lime, a weighed amount of which was allowed for each pit. Incidentally, scalding of goods can be due to the slaking of quicklime partially covered by stone and which may take 24 hours to slake properly.

Blast or the deposition of calcium carbonate on the grain of the skins is a constant source of annoyance in many tanneries, but it can be avoided to a large degree by taking certain simple precautions. For instance, goods should never be left with the grain side exposed and heaps must not be made in a draught. At night and weekends all heaps of limed goods should be well protected by means of sacking. These elementary precautions can prevent the formation of blast and save the tanner a good deal of money. When the goods are to be left two or three days untouched in the warm weather, then the sacking should always be dampened with

lime liquor. Some tanners take the extra precaution of covering the pelts with fleshes or splits from the band knife or Reeder machines before placing the sacking in position. Failing the use of linings which prevent the edges of pelts from drying and blasting, use can be made of skins flesh outwards.

The appearance of mould on pickled sheepskins, grains, etc., is often very troublesome and many recommendations have been made to avoid its appearance, which usually causes bad stains. Various disinfectants can be added to the rising or falling liquors and some of these have been specified in an earlier part of this series. The writer has found, however, that the mould is more prone to put in an appearance if the goods are stored in a warm place and far less likely to grow when the pickled pelts are stored in a cool, dry basement. In any case, it is never advisable to leave bundles of pickled pelts to remain untouched for longer than three or four months; not only is mould likely to put in an appearance, but fold marks and creases are liable to become set and extremely difficult to remove. This is a precaution well worth the labor involved in moving the goods.

An interesting problem arose some time ago in the finishing department of a tannery. The foreman finisher, who mixed the dopes for the spray booths, complained of lassitude, headaches and stomach trouble, obviously signs of some kind of poisoning.

The works manager at once investigated the trouble but made little headway. The ventilation in the room used for storing and mixing cellulose dopes was reasonably efficient and, moreover, the men working in the spray booths made no complaint. On close questioning of the foreman it was discovered that he first experienced trouble when preparing dope for a special order of kips for cheap uppers of an unusual vermilion shade. By concentrating on this single

shred of evidence it was eventually discovered that he used a sample drum of dope from a new manufacturer who was cutting into the field with competitive prices. A sample of the new finish and also a sample of the regular supply were sent to the laboratory and analyzed. The reports revealed that the new finish contained benzene, whereas the standard dope contained tuolene, which, although resembling benzene very closely, is less volatile, boils at a higher temperature and is far less toxic.

In his efforts to lower production costs, the manufacturer of the new finish had evidently used the cheapest solvents; in this case, benzene mixed with alcohol, together with other essential additives. Benzene is known to be a virulent blood poison. It lowers the red and white corpuscle count and leads to a general hemorrhage of the mucous membrane. Jordan, in his excellent book, "Technology of Solvents," states that the first signs of chronic benzene poisoning are lassitude, headaches, smarting eyes, vertigo, stomach troubles and emaciation. Other symptoms are bleeding of the mucous membranes of the mouth and nose, etc. Wher the use of the offending dope was discontinued, no recurrence of the trouble arose.

In passing it may be added that the cheapest finish does not always turn out to be the most economical.

With further reference to solvents, the writer has noticed that workers vary a good deal in their reactions to different solvents and some experience trouble if amyl acetate is inhaled, whereas others are completely unaffected. There is, however, such a thing as habituation and it has frequently been found that new workers, who are adversely affected by vapors from dopes during the first day or so, generally suffer no inconvenience when their system grows accustomed to the small percentage of vapor in the air. Men at the spray booths, that is presuming the latter are efficiently de-

signed, suffer less inconvenience from vapor than those who either mix it or handle it before spraying.

Still on the subject of finishing, the writer recently heard of a tanner who experienced difficulty in keeping his dopes blush-free and this in spite of the fact that he used only one brand of finish. Careful diagnosis of the complaint revealed some interesting facts. First of all, an analysis of the particular dope showed that it contained water-miscible solvents, such as alcohol, which, although themselves are not objectionable, may lead to trouble through the absorption of water and subsequent precipitation of the cellulose ester. It was also found that blushing most frequently occurred in the case of goods sprayed on a Saturday morning and that during dry warm spells blushing was never encountered. Another highly relevant fact was also unearthed. This was that quite frequently the steam in the spray rooms was turned off at midday on Saturday, so that goods finished up to 11:30 a. m., when the men began to clean up, were dried off at a much lower temperature than normal and consequently were liable to absorb moisture. In the opinion of the management, blushing was due to three contributory factors:

1. Presence of water-miscible solvents.
2. Periodic low temperature of drying-off.
3. Occasional presence of excessive moisture in goods before finishing.

The problem was placed before the manufacturer of the dope, who agreed to alter his formula so as to lessen the liability of the trouble recurring. He achieved his purpose by adding butyl alcohol, which is one of the best known protective agents against blushing.

The need for a special well lubricated leather possessing a high degree of electrical and thermal conductivity has been responsible for some interesting problems. Probably one of

the best methods of producing the desired results is to impregnate the leather with a graphite mixture. Chrome leather is the most suitable leather, owing to its ability to withstand high temperatures. The goods should be taken from the neutralizing bath, hydro-extracted or struck out by machine, then drummed in a steam heated drum until nice and warm. At this stage the colloidal graphite in aqueous dispersion, 115° F., added, and drumming continued until complete impregnation is obtained. In the case of curried leather, the colloidal graphite may be used as a dispersion in mineral oil and excellent results obtained. A writer in "The Industrial Chemist," October, 1938, stated: "Essentially, colloidal graphite is graphite reduced to a fineness where the individual particles, when dispersed in a fluid, are invisible by direct optical methods. That made by the Acheson process of colloidalizing will climb with facility with its carrier up a wick by capillary action, will flow, as a dispersion in water, through a filter paper, and has been successfully passed into the breathing tubes of mosquitoes. It shows active Brownian movement as a dispersion in water, while many of the particles show polychroic haloes when examined in the ultramicroscope.

"Colloidal graphite can be obtained as a dispersion in oil water or other liquid carriers. For diffusion into leather it is used in conjunction with castile soap, which lowers the surface tension in the interstices. Being chemically inert, it does not react with the soap, the tanning agents or with chemicals to which the treated leather may be brought in contact. Graphite is combustible only at high temperatures, above the ignition point of leather.

"The external appearance of a leather can be given the characteristic grey lustre of graphite by impregnation, coating, or both, and polishing the treated specimen by rubbing. It is an attractive finish, unaffected by heat and exposure,

and it may be inferred that stock so treated will have improved resistance to exposure and moisture.

"Graphite is electrically and thermally conductive and these qualities are imparted to the leather. It might be mentioned, incidentally, that paper has been treated with colloidal graphite for some time with these objects in mind. Dark and lustrous, graphite surfaces radiate heat and give leather a lubricating quality, which suggests its extension to applications where friction is a factor."

Sometimes the plant itself is responsible for troubles arising, and the writer heard some time ago of a tanner specializing in sumach skivers who complained of iron stains. Their presence entailed expensive clearing with dilute sulphuric acid and thereby increased the cost of production. The stains were mainly due to two causes:

1. Contact of partially tanned or completely tanned goods with iron equipment.
2. Condensation from iron pipes and other cold metallic surfaces dropping on to the goods.

In the case of the first mentioned it was found that the exposed iron parts of equipment could easily be protected with a rubber paint, preferably one made by dissolving chlorinated rubber in a chlorinated solvent. The film formed is able to withstand the action of acid, alkali and moisture and is particularly suitable for industrial applications. For maximum durability the chlorinated rubber is preferably mixed with a suitable plasticizer. Hercules recommends that chlorinated rubber be applied over a priming coat of the rubber and thermolyzed tung oil, or over an oil-resin primer. The following proportions are suggested:

Chlorinated rubber (20 cp), 20 parts.
Hercolyn, 8–12 parts.
Soft cumarone resin, 6–8 parts.

It is stated that Hercolyn, which is hydrogenated methyl

abietate, is particularly suitable as a plasticizer for chlorinated rubber for those applications where alkali resistance or moisture proofness are the prime considerations, or where the coating is to be submerged in liquids. All ironwork, including pipes, etc., can be protected by means of this rubber preparation, but in this particular case it was decided to provide a false ceiling to the tannery with cheap asbestos millboard, which at once overcame the problem of iron contaminated condensation. By taking these two simple and inexpensive precautions, the tanner managed to obtain almost complete immunity from stains.

All problems can be solved by the willing cooperation of the foreman with the works manager and chemist, who must work as a team. If any information is withheld, either for obstructional purposes or through carelessness, then it is extremely difficult, if not impossible, to arrive at a solution.

Reorganizing the Tannery on Efficiency Lines

In any worthwhile survey of methods and suggestions for improving the efficiency of the tannery, the first consideration must necessarily be given to personnel. Without the ready and sympathetic cooperation of the managers, foremen and staff it is exceedingly difficult if not impossible to insure a maximum output and to effect necessary economy measures. In the case of the latter it is a proven fact that sheer carelessness, rather than wilful neglect or ignorance, is the main reason why overheads cannot be kept down to an economic figure. Such little things as not attending promptly to leaks in the cold and hot water systems; failure to keep steam pipes properly lagged; failure to keep a careful check on weighing machines and other seemingly insignificant omissions are some of the many items which escape

attention and yet, collectively, make actual working expenses mount up.

The works superintendent may have a most imposing array of graphs pinned on his office wall, showing in several phases how the factory costs are being maintained at economic levels, but these do not represent the last word or provide any excuse for complacency. The works superintendent with strong actuarial propensities, who is content to stay in his office and devote a large proportion of his time to reports, surveys and other paper work, is not always doing the most profitable work for the tanner. In the writer's opinion, the administrative staff should spend its time in the factory seeing what is happening behind the scenes and not be content with merely cursory visits in the company of the departmental manager or charge hand. The works superintendent in an immaculate white overall is an imposing figure, but it is a bad sign if his overall is too white—at least for the tanner!

The cooperation between the works superintendent and the chemist must be a really workable one and they should not only have the utmost confidence in one another's ability, but be ready to listen sympathetically to suggestions. It usually happens that whereas the chemist is supposed to listen respectfully to suggestions from the superintendent, the latter is not always so willing to return the compliment when the chemist's recommendations are to do with the works. "Too theoretical" is so often the sole comment on many suggestions put up by the laboratory and although there may be a great deal of truth in the remark, it has a most discouraging effect and dampens the chemist's initiative and ardor to such a degree that he comes eventually to believe that it's far better for him to stick to his laboratory bench than go into the works and risk a direct snub from the superintendent. The writer has said on previous occa-

sions that the chemist who is content to keep inside the laboratory is not an asset to the tanner. The latter is losing the benefit of potentially valuable scientific initiative exercised on his behalf.

The question of reports is a vexed one. Some manufacturers seem to spend a large proportion of their time reading reports, some of them running to five or six quarto pages of typescript, which must have taken a lot of time to write. No one would deny that many of these contributions from the works office are excellent, but a large proportion are either quite unnecessary or could be useful condensed to a page or so. Reports can and, indeed, should be of the greatest value and guidance to the tanner, but they are apt to become a nuisance, if not a red herring drawn across the path to distract attention from inefficient management. In the writer's opinion, reports should be very brief and only issued when absolutely necessary. By adopting this rule they would carry more weight and assume a new importance in the eyes of the tanner or the board of directors.

A criticism which can safely be levelled against some works administrative officers is that they are liable to get into a groove through not making contact with other works or neglecting to keep abreast of scientific discoveries bearing on their particular problems. The works superintendent and his assistant should not only make periodic visits to other tanneries, but visit boot manufacturing and gloving plants, so as to discuss with operators some of the problems common to both industries. Then, again, they should make themselves acquainted with the progress being made in other unrelated industries as it sometimes happens that new discoveries, which may not at the time seem particularly relevant, can be usefully adapted to meet the tanner's own special needs.

An instance of this can readily be given. In the brewing

industry a protective coating is now being given to large metal tanks to protect them against the corrosive effects of mineral and organic acids. This coating consists of a phenolic resin which is sprayed on to the metal to form a coating 3/1000 inch thick and weighing only 1/20th ounce per square foot of treated surface. The resin is baked by means of hot air until it is properly cured or polymerized. Now it occurs to the writer that this protective finish is just what is needed to protect metal work in the tannery, which is often so badly corroded through the action of both mineral and organic acids. Obviously here is a need for investigation. This instance of the promising results which can be obtained by making oneself acquainted with the methods of tackling other industries' problems is only one out of dozens which could readily be cited. Although it may seem that every trade has its own very peculiar and exclusive problems, a little careful probing will often reveal that, in a slightly different form, that same problem is receiving attention and may be solved by another totally unrelated industry.

Keeping up to date is important. An idea which is carried out in some European countries is to send picked men to colleges and universities for "refresher" courses. This is not only useful in so far as it provides them with new knowledge, but also broadens their outlook and encourages them to look at their own particular jobs in a different perspective. A fresh, imaginative outlook is valuable to the tanner, especially when backed up with real practical experience in his own works.

XI

SPECIALTY LEATHERS

The tanner specializing in any particular class of light leather can, by a little careful planning, which need not involve much expense in the adaptation of existing plant, add to his range of goods and so break in on a new market at the flowtide. This ability to produce new lines is of the greatest importance to the tanner and it certainly pays him to be conversant with the processes and recipes for all types of light leather, particularly new or improved methods of producing popular or potentially popular goods. Fashion is very fickle and the manufacturer who may be the acknowledged leader in one line, say willow calf and glace kid, may find that one season these hang fire, whereas box calf and dull finished or mat kid are in great demand. If he is blessed with a real live works manager or superintendent he may be able to direct some of his goods into the new channels, but in many cases he is handicapped by lack of real practical knowledge and for this reason forced to build up new methods by the painfully slow method of small scale experimentation.

There are many excellent books devoted to the general principles of light leather manufacture, but it must be readily confessed that there is a real dearth of practical manuals giving tested recipes and short cuts to results. The present series represents an attempt to fill the breach and so provide the

tanner with data he can use as a basis for his own recipes. It must, of course, be realized that no two tanners have exactly the same ideas as to what constitutes the best and most economical method of producing a certain type of goods; indeed, a universal recipe would not work out well at all, as generous allowances have to be made for the particular kind of hides or skins employed, the idiosyncrasies of the plant, water, etc. The fundamental principles laid down in the methods described in detail by the author will, he maintains, prove of considerable value to tanners anxious to evolve their own individual methods. A wide field is covered in the series and the most important classes of leather—sheep, goat, calf, kips, kangaroo, vellum, and parchment—are described.

Hat Lining Skivers

The size of a pack of goods varies quite considerably, but for normal sized tan paddle wheels with a capacity of 1,500 gallons, 45–47 dozen skivers is considered an average load. It is, of course, uneconomical to process smaller quantities of goods and the general procedure in the trade is to make up a small order of grains with skins of another pack which have been marked with a distinguishing punch hole or distinctive brand in the neck or butt. This mark enables the crust sorter to pick out the branded skins and so isolate the original order. Tan paddles of 1,500 gallons are considered to be of average size in Great Britain, but the writer understands that on the Continent and in America a smaller capacity is preferred.

Quality of Grains

Grains for hat linings must be of good quality and free from "cockle" or "colt." The former defect renders the

goods quite unsuitable for hat bands as, when tanned, the "cockly" parts dry out hard and harsh and also gather up in a characteristic manner. Grains must not show traces of weak grain, very prevalent in summer pelts, pin holes, barbed wire scratches or flay marks. They must also be fairly large in area and heavy in weight, preference being given to long skins, butt to neck, rather than square shaped ones, as the former enable more bands to be cut and thus are more profitable to work. These are small points but, nevertheless, they are certainly important, and, if carefully considered, insure a larger margin of profit.

It is essential that the substance should not show very much variation and be uniform throughout. Falling off in thickness towards the belly means that the waste will be considerable. While band knife splitting does not leave the characteristic "ribbed" markings of the reciprocating blade type of machine, such as the "Reader," it cannot produce such a uniform split and, in the writer's opinion, the "Reader" machine gives the best results. With both band knife and "Reader" it is, however, necessary that the pelts should be well limed and firm enough to cut easily. This means that liming must be fairly thorough, at least a week, and goods allowed to settle for a day before splitting. Four days in a mellow lime, followed by three days in a sharp sulphide lime, is recommended. After machine fleshing the goods must be piled up in heaps of 400 or so and left for 24 hours before sorting. The "splitters" take their particular grades and "slick" them out with small metal slickers, so that all creases are pushed out and the pelts lie perfectly smooth and flat. Slicking out is really quite an important operation and must be carried out very thoroughly, otherwise the accuracy or uniformity of splitting will suffer.

The grains should be removed from the machines to the puer shop without delay, otherwise they will harden and take

longer to become really flaccid in the bate. The best procedure is to make up a load, that is, enough to fill the deliming wheel as soon as enough pelts have been split and not to wait until the end of the day for the bulk of the goods.

Deliming

Generally the deliming wheel is not as large as the sumach tan wheel and the pack of 45 dozen may have to be processed in two lots. For a deliming wheel of 1,000 gallons, three pints of hydrochloric acid, diluted with one pail of water, is sufficient to remove the bulk of the lime and yet keep the goods slightly alkaline. The best procedure is to run the grains in the paddle in running water for one hour, then add the diluted acid and run for two hours. Block up exit and continue processing for half an hour in running water. There does not seem any advantage in using the more expensive organic acids in place of hydrochloric for this work and the writer prefers the use of acid to the mild alkalies often recommended for the same purpose.

Puering

At the risk of appearing old fashioned, the writer maintains that natural dog excrement is by far the finest bate for this class of work. One bucket of dung in the exhausted puer at 110° F. for half to three-quarters of an hour, depending on the condition of the goods, should be sufficient to bring them down to a nice silky condition.

Scudding

This must be carried out very thoroughly, otherwise the grain will never show up clear and fresh looking. It is important that all traces of pigment, fat, and traces of "downy

wool" should be completely removed. Hand scudding is to be preferred, but if ruled out on the grounds of economy, then the grains should be passed through the machine twice, taking particular care that pressure is put on so that they are made to keep a good elongated shape.

Drenching

Instead of using the traditional bran drench for these goods, the writer prefers a 1 per cent lactic and ½ per cent acetic solution. Grains should be paddled in this for 20 minutes, then transferred straight to the rising or pickling wheels.

Rising or Pickling

Salt liquor made up to 10° Twaddle is acidified with one gallon sulphuric acid per 1,000 gallons liquor. Goods are paddled for half an hour and then pulled out and dropped in a tank containing strong brine, 20° Twaddle, and allowed to fall for at least 20 minutes. They are now ready for tanning.

Tanning

There are, of course, various methods of tanning grains for hat leathers, but sumach tanning is by far the best known and will, therefore, be described first.

The pack of goods should be first run in a paddle containing exhausted tan liquor which, however, holds sufficient tannin to strike the grain and prevent case hardening and harshness of any kind. It is essential that the grain surface should be smooth and soft, otherwise the linings will have to be relegated to a lower and cheaper grade. Four buckets of salt are added to the spent liquor to keep down swelling. Grains should enter spent tan not later than 10:30 in the

morning. Paddles run until after lunch, 2:00 p. m., when by that time the new tan liquor has been made up. The paddle requires 6½ cwt. of best sumach (tannin content 25–27 per cent), five buckets of salt and one pint of vitriol. Temperature of liquor 98° F. on entry of goods. The liquor should be thoroughly stirred up before entry of the pack, and this is best done with proper wooden plungers. Goods must be allowed to run until 6:00 p.m. and then next morning the paddle requires starting up at 8 and running until 12 noon and this program is continued for one week. Although grains can be struck through in less time than one week, it is advisable to allow them the maximum length of time so as to plump them up.

When it is desired to reduce the cost of the tannage, myrobalans extract may be substituted for two-thirds of the sumach. A suitable method is to run the goods in the exhausted tan liquor as above, only this time, of course, it will contain myrobalans as well as sumach, then make up a new liquor with 2½ cwt. sumach, salt, and acid as before and five gallons of myrobalans extract. Run as before and next day add another five gallons of extract and the day after another five gallons and continue running until the goods are thoroughly tanned. This recipe can, of course, be adapted to meet requirements and, if necessary, quebracho may be substituted for some of the myrobalans towards the end of the tannage.

Where a perfectly white or cream leather is required, then a mixture of sumach extract and synthetic tannin should be used.

Rinsing and Drying

Tanned goods must be individually rinsed in a tank of cold water and packed on large horses and allowed to drain

for 12 hours. They should then be hoisted up to the drying sheds and hung up on hooks. Heat should not be used, except for periods in the depth of winter, when it is impossible to dry the grains without it. During the warm weather the louvres must be kept wide open, but as soon as the goods are dry they should be taken down and stacked in heaps. It is recommended that during drying the skins should be pulled out, taking care, of course, not to drag them off their hooks, so that the full area can be exposed on the sorting table in the crust warehouse. Tanners usually see that the goods are stacked in neat heaps, not too high as they may heat, and that small weights are placed on the top of the heap on the neck, shanks, and butt, so as to keep the skivers as flat as possible.

All greasy skins require degreasing before sorting and in most tanneries goods are sent to the petroleum degreasing tanks, irrespective of whether they show traces of grease or not.

Sorting in the Crust

Sorting is a tricky job and must be carried out by experienced and intelligent men. A good north light is necessary, in order that every defect is at once visible to the sorter, who is expected to achieve a high degree of accuracy in the classification of the various grades. In the case of hat leathers, the flaws he has to pay particular attention to are:

Weak grain.
Thin impoverished goods.
Rib or splitting marks.
Cockle.
Uneven substance.

He must also see that the weight of the skivers for hat linings conform to the requirements of the hat leather de-

partment. Color is also of importance in the case of light shades and dark skins should be kept on one side to fulfill orders for dark browns. The poorest skins in the hatter class go for printed orders and the finest quality for flat finishes.

Wetting Down and Clearing

Goods should be wetted down in warm water 100° F. in a drum or paddle and then cleared with weak sulphuric acid, ¼% on the crust weight of goods. After half an hour they should be thoroughly washed in running water and then allowed to drain ready for dyeing.

Dyeing

Various shades of brown are the most popular for hat bands and they must be extremely fast to wet rubbing and perspiration. Dyewood extracts should be used wherever practical and it is possible to obtain a wide range of shades with such extracts as peachwood, cutch, sumach extract, etc., either alone or in combination with titanium potassium oxalate, tartar emetic, etc. A popular brown shade can be obtained by "bottoming" with sumach extract, cutch and T.P.O. and dyeing with chrysoidine.

FOR 100 LBS. CRUST LEATHER

Bottom (2½ lbs, sumach extract paste)
(2 lbs. cutch)
4 ozs. Titanium potassium oxalate.

Run the goods in the mixed extracts in the drum for three-quarters of an hour, then add the mordant to the exhausted liquor and continue for another 20 minutes. Transfer to another drum containing the dye liquor at 110° F.

Dye 12 ozs. suitable basic brown dye.

Process for half an hour or until correct shade is obtained, then add ½ oz. potassium bichromate dissolved in water to fasten the color. This will also sadden the shade slightly and due allowance must therefore be made for this. Some tanners top off the basic dye with a little acid dye and then use the bichromate. They claim that a faster and richer color results.

After dyeing, the goods need well rinsing in cold water and laying up ready for striking out. The flesh or split side should only be struck out and the goods given a quick coating on the flesh or split side with a weak solution of starch made up with 2% wheaten starch. The skivers then need horsing up flesh to flesh and leaving for six hours. The grain side can then be struck out and the goods strained in the usual way.

Finishing

Once off the boards the skivers need fluffing and trimming and then seasoning. This is best done with a starch or Irish Moss solution containing a small quantity of glycerine and best curd soap. About 2% starch, ½% glycerine and ½% soap is recommended for seasoning flat finished bands. Another useful formula is: 1½ lbs. linseed, 3½ gallons water, 2 pints milk and 4 ozs. glycerine. One or two applications, drying between different applications, may be necessary to achieve the desired results. After seasoning the goods need rolling and reseasoning and lightly glazing and ironing with a warm iron. In the case of printed goods a good procedure is to season, roll, damp down in blankets overnight, emboss on the Sheridan or other suitable machine next morning, roll to cut up grain, air off and light glaze. The secret of success in finishing this class of goods is to use a very simple sea-

soning formula and to see that the grain is never clogged up and so made to have an artificial appearance.

Skivers for Fancy Goods and Bookbinding

Pelts for fancy goods should be of medium quality and slight grain imperfections, such as barbed wire scratches, scars, weak grain, etc., which are not too noticeable, need not necessarily render the skins unsuitable for this class of work as a large percentage of skivers for cheap bags, novelties of all kinds and even bookbinding leathers are embossed. For best bookbinding purposes, however, a very high quality is essential and grain defects would at once render them unsuitable for this purpose. Pelts affected with cockle (although obviously a great deal of discretion must be shown here) can often be adequately covered or disguised with a bold plated grain. So-called colty goods are unsuitable as the skivers are harsh and only suitable for the cheapest embossed grades.

Fresh skins from the hide and skin markets can be fellmongered straight away without preliminary washing, although in the case of badly soiled skins it is advisable to give them a soak to cleanse both flesh and wool. The writer advises soaking the goods in a pit containing ½–1 per cent sodium bisulphite on the weight of skins. This will have no injurious effect on the wool; indeed, it will improve its color, and by reason of its antiseptic properties help to preserve the pelt from bacterial damage. After soaking for 8 hours, the goods should be centrifuged for 3 minutes and then spread out carefully in piles ready for painting. The most suitable hydro-extractor for this work is the 48-inch machine, which is large enough to handle reasonably sized packs.

For sheepskins the most suitable depilatory is undoubtedly a paste made up of sodium sulphide and lime. Other processes of depilation, such as result through sweating,

fermentation, and bacterial and enzymic action, are still in the experimental stage and unless very carefully controlled are dangerous. This does not, of course, mean to say that they are of no commercial value. On the contrary, many of the latest methods of depilation give excellent results and have several important advantages over the more familiar processes, particularly as they are without injurious effect on the wool. Sulphide and lime pastes destroy the ends of the wool fibres and thus injure the wool, especially if an excess of depilatory is used and capillary creeping takes place. A recent Italian patent is of particular interest, as by incorporating gum tragasol with the sulphide it tends to reduce or control its violent action. It is claimed that a mixture of the gum and concentrated sulphide produces a smooth, easily workable paste.

The writer favors the use of hydrated lime of a specified mesh on account of its uniformity. It is, however, more economical to use good slaked lime and to sieve it so that a powder is obtained of 100–200 mesh. This lends itself very well to the production of a smooth paste. It is a great pity that tanners generally do not make sufficient use of the sieve, which can often be of such great assistance in helping to regulate the physical characteristics of a product. The most useful meshes are 25, 50, 100, and 200.

A mixture of 40 lbs. sodium sulphide, 45 lbs. hydrated lime, and 20 gallons water will produce a very satisfactory depilatory. Run the water into a sound wooden tub and throw in the sulphide crystals and stir until thoroughly dissolved. It helps considerably if the temperature of the water is about 60° C. Add the lime slowly and with constant stirring and allow the mixture to cool to normal temperature before using. This is vitally important as use of a warm depilatory may have a most disastrous swelling action on the wool. Instead of using the above formula, some tanners

prefer to make use of a stock solution of sulphide. This is of varying strength, usually about 15–20 per cent of the procedure recommended is to add slaked or hydrated lime to this until a paste of the correct consistency is obtained. It may be added that a dozen different recipes are available, any one of which will, in skilled hands, prove efficient.

Depilation should be carried out on a trestle table and organized so that as nearly as possible each skin receives approximately the same amount of depilatory. Too much sulphide is almost as bad as too little and results in excessive swelling of the pelt, whereas too little simply leaves the wool tight and the pelt flat. In the painting operation great care must be taken to see that the wool is kept clean and free from depilatory.

In dealing with large quantities of skins, a great impetus to efficiency can be given by attention to small details, such as adjusting the height of the table so that it is comfortable and convenient to work at. The position of the worker in relation to his work, and also the position of the heaps of skins awaiting depilation, all these are important factors, and in any attempt which may be made to economize movements and eliminate unnecessary exertion they should be very carefully considered. A few experiments will soon show how depilation can be so arranged that a greater output is insured, and the works foreman is fully capable of evolving improvements if he is encouraged to do so.

Wool should be thoroughly washed and then hydro-extracted. Using a 42-inch machine, it is possible to handle 3 to 4 cwts. of wool. A short run of 5–6 minutes is usually sufficient to remove 20–30 per cent moisture. The wool is then ready for the stove for drying.

After rubbing, the goods should be thrown into a mellow lime, that is, one a week old, and allowed to remain 3 days with one good draw a day. The liquor must be thoroughly

plunged up or otherwise agitated before replacing the goods. It is necessary to lime the goods thoroughly so that they are nice and plump. Unless the skin is firm, it will not cut clean during splitting. The writer favors a week's liming and this should preferably consist of 3 days in a used or mellow lime and 4 days in a fresh sharp liquor. It is sometimes advisable to add sulphide to the lime, especially if the goods are stale, green or poor quality. For fresh, good quality skins a straight liming is in every way preferable.

A procedure recommended by the author for sulphide liming is as follows: After de-wooling, the pelts are first cast, that is, sorted into various grades according to size, weight and quality, then thrown into a mellow lime liquor with a total alkalinity of 6, this figure representing the number of ccs. of N/10 HCl required to neutralize 10 ccs. of liquor. After at least six draws, that is, two draws a day in this liquor, the goods should be switched over to a pit containing a fresh sulphide liquor made up with 15 buckets slaked lime and 5 buckets of sodium sulphide liquor, 26° Twaddle. The alkalinity of the liquor should be about 9. Usually three days, 2 draws a day in this liquor, is sufficient to plump the goods, but if necessary, 2 more buckets of sulphide can be added after the first day.

Where fresh liming is required, a considerable surplus of lime should be used and 1½ cwt. of quicklime for an average pit is generally sufficient. After 2–3 days in a used or mellow liquor with 1 draw a day, the liming should be continued for 4 days in the sharp lime with 1 draw a day. To gain the maximum benefit from a new lime it is advisable to plunge or agitate the liquor thoroughly before throwing back the goods.

Paddle liming is now used to a greater extent in the United Kingdom and is certainly a good deal quicker than pit work. It has, however, the disadvantage of being some-

what harsh on the grain, although the writer is aware that this is hotly denied by a large number of tanners in the United States. Excessive paddling or movement of the goods should be avoided and agitation kept down to a minimum. Working at an alkalinity of 9-0 is capable of excellent results and usually the lime contains sulphide, the amount depending on the type of goods being processed.

After liming, the goods are pieced (that is, unnecessary offal cut off), then fleshed by machine and cobbed (odd fragments of wool removed) and finally scudded. The latter operation can be carried out after steeping goods in warm water for a few minutes. Nowadays scudding can be carried out by machine and is rarely done by hand. For cheap orders it is not economical to scud at this stage.

When goods are ready for splitting they should be piled up and allowed 24–36 hours to settle properly. This is most important, as otherwise the pelts will not have the necessary degree of firmness and knife cuts will not be clean. Sorting comes next and here great care is necessary to insure accurate grading. The splitter depends upon the accuracy of the sorter in setting his gauge for thickness and good sorting saves money and insures smooth working of the department.

The grains are taken from the machine and sent at once to the puering shop, where they are washed in running water in a paddle for 15 minutes. At the end of that time 2 quarts of hydrochloric acid are added (properly diluted with 1 gallon water) and processing continued until the cut surface of the grain is faintly alkaline to phenolphthalein. In the case of bookbinding skivers it is preferable to use formic acid instead of the cheaper mineral acid. Puering should be carried out with a good enzyme bate at 98–100° F. for ½ to ¾ hour, according to the weight and condition of goods. Empirical formula is really worthless for this operation as the overseer must use his own judgment and alter the con-

centration of enzymic bate to insure the best results. After bating, a short washing in cold running water is necessary to remove all trace of bate. If necessary, the goods can be machine scudded so as to insure that all filth, now easily removed as it is emulsified by the bate, is removed from the pores. Scudding is to be recommended, as it renders the grain clean and better able to take light colors, should this be desired.

Although drenching is not always regarded as necessary, the writer considers that it does definitely contribute to the quality of the grains and should, therefore, not be omitted. The temperature of the water must be 30° C. and the amount of bran, 1 bucket to 10 dozen average grains. Twenty-four hours in the drench paddles, without agitation of any kind, is sufficient to achieve the desired result.

Rising is usually carried out with either sulphuric or hydrochloric acid, but in the case of bookbinding grains it is advisable to substitute formic acid. The proportions recommended for sulphuric acid are: Brine 10° Twaddle containing 7.5 D. O. V. (distilled oil of vitriol) per 100 gallons of liquor. When using hydrochloric acid, 9 lbs. commercial acid should be added to 100 gallons of brine, 10° Twaddle. Formic acid pickling can be carried out with 10 lbs. commercial acid per 100 gallons brine, 10° Twaddle. In all cases, rising or pickling should take 30 minutes.

If grains are to be stored they should be fallen in a 22–24° Twaddle brine for 25–30 minutes, then drained and stacked in dozens in a cool, dry place. Some tanners sort grains in the pickling shop and this is a good plan, as they are white and clean and every defect shows up extremely well.

Sumach tanning is generally preferred in the United Kingdom for skivers, although this is frequently adapted so as to economize in the use of the ground leaf, which is an ex-

pensive tanning material. Straight sumach tannage is certainly preferable for the best bookbinding leather and it is advisable not to use any mineral acid for this class of goods. For an ordinary sumach tannage the goods should be put into a large paddle containing spent liquor holding 80 lbs. salt. After 2½ hours' running the grains should be drawn ready for the strong liquor. This is made up of 100 lbs. salt and 4 cwt. best sumach for 1,500 gallons water, which is the normal capacity of a large wheel. This should process about 45 dozen average grains. There is no necessity to run the wheel continuously and if it is run for 5 hours a day, this is sufficient. About 3–4 days will complete the tannage. Goods then need rinsing in cold water to remove bits of sumach, draining ready for removal to the drying sheds. Hydro-extraction is not advisable, as although it shortens the period of drying very considerably, it is liable to cause creases which are difficult to remove. In the case of bookbinding leathers, the addition of 2 pints of formic acid to the sumach liquor is recommended, and for ordinary goods 1 pint of sulphuric acid.

An alternative and cheaper method of tanning consists of running the goods in a liquor made up originally of myrobalans and quebracho. For a paddle containing 1,500 gallons water use 2 cwt. ground myrobs. and 10 gallons sulphited quebracho extract. This should be sufficient to make up the wheel for 45–50 dozen grains. Leach the ground myrobalans in half the quantity of water at 150° F. Stir well for several minutes, then add 100 lbs. of salt and ½ pint concentrated sulphuric acid together with 2 gallons quebracho, the remainder being added next day. The green goods should be processed first in a used or mellow liquor for 12 hours and then transferred to a new liquor made up as above. When the grains are just tanned, which should take about 3–4 days, they must then be sumached in a pad-

dle or drum. This can be carried out by using 1½ cwt. of sumach to a pack. In the author's opinion, it is preferable to give a sumach bath at the end of the combination tannage rather than add the sumach to the paddle wheel containing other types of tannins. In place of quebracho, any other cheap and concentrated extract can be used.

During the latter stages of drying the goods must be opened out so that the maximum area is obtained. When thoroughly dry they should be sorted and then sent to the dye-house.

For bookbinding leathers the writer favors dyeing first with acid colors and then topping off with basic colors. The amount of dye in each case depends on the penetration desired. Dyeing should be carried out at 112° F. for the acid leveling color. Run the goods in the full color for 15 minutes without acid, then add formic (three-quarters the weight of dye used) and continue processing for 40–45 minutes. Remove goods from the liquor, rinse in cold water and then top with suitable basic dyes. The latter should be dissolved in water acidified with a little acetic acid and added to the dye water, 95° F., in two portions. The addition of half the quantity of formic acid used for the acid dye is recommended. This method of dyeing, although a little more complicated and certainly longer than is customary for skivers, is recommended for all bookbinding leathers, as the resulting color is very fast to rubbing and has excellent penetration.

For general dyeing of skivers the writer recommends a temperature of 45° C. About 1 per cent sulphuric acid on the sammied weight is usually sufficient and this should be added 20 minutes after dyeing. The dye is preferably added in two portions, the second being run in directly after the acid. The dyeing can be carried out equally well in drum and paddle, but the latter is advisable, as there is less likeli-

hood of goods getting torn. On the other hand, drum dyeing is economical and quicker. The amount of water to be used must vary a good deal, but between 500–600 per cent on the sammied weight is considered to be advisable. When using acid dyes, no mordanting is required, although for basic dyes it is advisable to mordant with ½ per cent tartar emetic and wash well before dyeing. M. C. Lamb recommends paddle dyeing where a large pack has to be dyed one shade. He is in favor of filling up the paddle with water at 55° C. and then throwing in the goods. The fall in temperature is about 5–10 degrees, and just right for dyeing. The dye should not be added until the skivers are thoroughly wetted and evenly dispersed throughout the volume of water.

After dyeing, the goods should be washed up in water containing 0.25 per cent sodium acetate, rinsed thoroughly and struck out ready for straining on boards or by toggle frames.

When perfectly dry, the skivers are ready for finishing. There are, of course, hundreds of different methods of finishing available for skivers, but the writer will discuss first the ordinary method of simple seasoning as distinct from pigment finishing. Seasoning is usually preferred for bookbinding leathers and the best fancy goods. A very serviceable finish consists of 3½ ounces of best Argentine casein and 7 ounces of egg albumen to the gallon. The casein should be dissolved in a weak borax solution, using 8 ounces of borax to the pound of casein. The best way to dissolve it is to soak the casein in water overnight, heat it to 50° C. next morning with constant stirring. Then add to it the borax dissolved in boiling water and stir thoroughly until solution takes place. When perfectly cold, or just tepid, add the egg albumen.

Skivers should be lightly perched, then seasoned with a brush, dried, rolled or glazed and then printed. Two coat-

ings of seasoning may be used if considered necessary, but these should be light. For smooth finished bookbinding skivers a finish somewhat similar to one used for hat leathers is sometimes used.

6¼ gallons water.
21 ounces Chinese Isinglass.
2¾ ounces tartaric acid.
60 ounces methylated spirits.
¼ ounce chipped soap.

In the case of pigment finishes now usually preferred to seasoning mixtures on account of their very high covering powers, the procedure is usually fairly simple. The goods are lightly perched, then sprayed with the water pigment, usually a casein bound preparation. Cellulose finishes are not generally employed for skivers owing to their high cost. It must be realized that as all types of skivers sell cheaply, finishing operations must necessarily be cut down to a minimum of time and cost. It is not possible to describe in detail the finishing of the many different kinds of skivers, such as paste grains, piano leathers, etc., but the concise data given will be found of value as a general guide and may be adapted to meet special requirements. For finishing the flesh side of skivers, use should be made of one of the mosses, preferably sodium alginate or Irish Moss, in a 5–7½ per cent solution. When it is required to fill up defects in the grain of skivers, the same solution may be used to great advantage.

XII

ROUGH BASILS FOR PRINTING

HOME tanned and imported rough tanned basils are extensively used for printing, the finished goods being used in the manufacture of cheap bags, novelties of all kinds and, to a certain extent, for low price shoe and slipper work. Basils recommended for this purpose should be of heavy or medium weight. Disfiguring faults, such as scabs, scratches, cockle, scars of various kinds, flay marks, etc., most of which can be adequately covered by bold printing, do not render the goods unsuitable for printing and indeed this is often the only satisfactory outlet for such goods.

In Europe, quebracho and myrobalans, also cheap synthetic tanning materials, are widely utilized on account of their relative cheapness. It is natural that in the production of cheap grade leathers the economics of production should be given premier consideration. Where possible the use of natural tannins is to be preferred as the resultant leather is plump, takes a nice deep print without getting hard and dyes easily and quickly with acid dyes. Paddle tanning is generally preferred when using natural tannins and the drum is reserved for synthetic materials, but this preference is merely arbitrary on the part of English tanners. Excellent results can be obtained by paddle tanning, but it is as well to point out that when highly astringent tannins, such as quebracho, are employed for reasons of economy and speed, it is advis-

able to ease-up the agitation of goods during the early stages of tanning owing to the danger of case hardening and a whole heap of trouble. For this reason it is considered advisable by many competent tanners to use the paddle wheel in preference to the drum, but, when the latter is employed to start the process with tannins rich in non-tans and add the astringent extract when the green goods have just taken on the brownish tint of the tannin, that is, when it has struck.

A useful compromise which the writer knows will give excellent results is to drum the pickled goods in a cheap, but not too acid, synthetic tanning material and when the goods are half tanned to finish off with a good blend of tannins, a mixture of gambier, myrobalans and quebracho is recommended. Apart from the question of cost, and quebracho is one of the most economical tannins in use today. It is a very valuable one, especially for goods of this kind which must be given a firm, strong grain able to take accurately the impression from the embossing plate and to retain the new grain as long as possible.

Rough basils are usually picked out in the limeyard by the sorter who examines the pelts from the fellmonger. The following defects are the ones most often responsible for rejecting goods and their classification as rough basils. The main thing to bear in mind is that the requirement of the printer is a good area skin of medium or heavy weight and even substance, the latter qualification being most important. Where the grain damage is slight or lends itself to disguise by means of a boldly printed grain, then it does not matter very much. On the other hand, if the grain damage is due to bacterial action which is responsible for a break-down of the pelt, then it would be useless to process the pelt and it is only suitable for boiling down for glue.

It is false economy to process pelts where it appears at all doubtful regarding their ability to produce commercially use-

ful leather. It should be remembered that once tanned, grossly inferior goods can no longer be used as glue stock and tanned offal is practically valueless. Table I gives some idea of the main defects to be found in fellmongered pelts and how far they should influence the sorter.

TABLE I
MOST COMMON DEFECTS IN SHEEPSKINS FROM THE FELLMONGER AND QUALIFYING REMARKS

COLT—Provided the goods are not too hard, horny and swollen, they are usually found workable. Liming must be cut down to a minimum and puering time reduced. Colty goods make rather harsh leather, but this need not matter very much if the substance is level and the leather itself possesses reasonable strength.

COCKLE—This is really a nutritional disorder and appears to develop as the fleece grows. It shows most in the skins of sheep just ready for shearing or newly shorn. The small rounded nodules can usually be fairly easily masked by a good embossed grain, but where there is a decided falling off in substance down the belly then it is doubtful whether it would be economic to use the pelts for printing, which requires a full and even substance for the best results.

SCABS AND SCARS—Deep rooted scabs from boil-like skin infections show as holes when the goods are tanned, but barbed wire and thorn scratches are not serious and may be covered by the printed grain.

FLAY MARKS—This defect is responsible for a tremendous writing down in the value of sheep skins. If the flay marks do not penetrate too deeply or encroach too far on the area of the pelts, then the goods may be worked quite profitably, but where the workable area is small it is unprofitable to proceed and the pelts should be used for glue stock.

INSECT OR RODENT DAMAGE—This is not so serious as bacterial damage, but very often the two go together.

WASTE DUE TO BACTERIAL ACTION—Stale, badly wasted pelts are only suitable for glue. Even if what appears to be an appreciable area is unaffected, the pelts frequently break down when processed and are quite useless.

FALLEN SKINS—The pelts of animals which have died from natural causes are usually under-nourished and thin. They are useless for embossed goods owing to lack of substance, but may be worked for cheap shoe linings, etc.

The general processing of rough basils for printing does not differ materially from the practical data given by the writer for roans intended for hat leather, except, as stated above, there is no need to carry liming so far and puering time should be reduced to a minimum.

Sorting Goods in the Pickle

Pickled goods should be drummed in a 10 per cent brine solution before tanning by either the drum or paddle method. Running in the brine washes out a certain amount of excess acid and also removes any creases or folds which may be present in stored goods. It is a good practice for the foreman of the salt shop, as it is commonly called in England, to go through the pack of goods intended for basils and to throw out any obvious rejects. These can be de-pickled and sold as glue stock. Some tanners consider this extra scrutiny worth while, but it should be pointed out that skins which may be unsuitable for printing may, when roughly tanned, prove suitable for aprons, leggings, and gloves to be worn in the tannery.

Tanning Procedure

Twenty minutes drumming in brine is sufficient and after that the goods are ready for tanning. The first method which will be considered is paddle tanning, making use of a large paddle able to process 45 doz. common roans (capacity of paddle approx. 1,500 gals.). The strength of the tannin ready for the green goods should be 6–7 grms. tannin per

litre and the tannin should be made up of myrobalans and quebracho, using at this stage three times as much of the former as the latter. To reduce swelling, 45–50 lbs. of salt should be added to the weak tanning liquor. The paddle should be run not more than four hours a day, preferably two hours at a time throughout the eight-hour shift. At the end of five days the strength of the liquor should be brought up to 15 grms. per litre of tannin, that is, full strength and tanning continued for another three to four days or until the goods are thoroughly tanned. Instead of strengthening up the original liquor it is recommended to use two batteries of paddles.

No. 1. Used liquor made up to six or seven grms. of tannin, salt added, to receive pickled goods. This liquor was previously a strong one and after the pack has passed through it is run away and strong solution, 15 grms. per litre, made up to receive goods from the weak liquor.

No. 2. This is a fresh liquor, 15 grms. tannin per litre, but containing no salt. Tanning is completed in this liquor.

Tanning with Syntans

An excellent and very economical method of tanning by suspension is carried out in some tanneries in Europe. The pickled goods are washed up in 10 per cent brine for 15 minutes, then suspended in a large vat containing 10 grms. per litre of a cheap synthetic tannin of the Neradol type and 2 grms. per litre of salt. After 12 to 24 hours they are removed and drummed in a fairly strong mixed tanning liquor, 25 grms. per litre, quebracho and myrobalans; no salt used until they are tanned. The writer recommends the addition of a little light mineral oil to the tanning liquor to reduce surface tension and help to produce a smooth, soft

grain which will take a clear and true print from the embossing plates. Goods tanned in this way will dye fairly easily, but it is as well to give them a run in warm sumach liquor before dyeing so that the acid dyes will strike evenly. This combination tannage is calculated to produce commercially good leather in three to four days, shorter period if drumming time is extended, but this is not advisable and the best results are obtained by drumming for short periods at regular intervals throughout the day.

Most of the modern synthetic tanning materials may be used very successfully and economically in the drum, employing 3 per cent tanning material and 150 per cent water on the weight of the goods. In some cases it is advisable to de-pickle the goods, or to use goods straight from the drench or bate. To the exhausted syntan liquor the requisite amounts of vegetable extracts can be added in three or four different portions. A typical example of this method of tanning common basils and roans, etc., is given by Geigy for their Sellatan.

"The pelts are put into a drum with 150 per cent water on the pelt weight (de-pickled) and 2 per cent Sellatan. After 30 minutes a further 2 per cent of Sellatan is added and running is continued for three hours. The skins by this time should be completely penetrated and ready for finishing with extracts. In order to complete the tannage, 38 to 40 per cent tans of an extract of 30 deg. Bé., according to the state of the pelts, should be added to the exhausted Sellatan liquor. For sheep, Geigy recommends a mixture of 15 per cent quebracho and 15 per cent mimosa bark extract (liquid). The skins are usually tanned through in six hours and it is better to leave overnight in the drum." Pelts which are first colored with synthetic tannin take up the tanning material so intensively that the remaining liquor in the case of drum tanning is absolutely exhausted and can be drained off.

Using Straight Vegetable Tanning Extracts

Where it is desired to use straight vegetable tannings for drum tannage and not to employ syntans, then the following procedure is recommended for common basils for printing: Drum the goods in a 5 per cent salt solution, using 150 per cent water on the weight of goods, for 15 minutes. Then add a blended extract made up of 60 per cent myrobalans, 15 per cent hemlock of mimosa and 25 per cent sulphited quebracho to give a solution containing 15 grms. tannin per litre. After two hours' drumming the color will have struck and the drum should then be stopped and the goods poked under the surface of the liquor and left for three hours. The drum can then be started up and the liquor strengthened by running extract through the hollow axle to bring the strength of the solution up to 30 grms. per litre of tannin.

Two to three hours' drumming should be sufficient to get the tanning well into the skin. Next day the liquor can be strengthened to increase the strength up to 45 grms. per litre, using this time a greater proportion of quebracho, say a mixture of 65 per cent quebracho, and 35 per cent mixed tannins. Two to three days is usually sufficient to insure a thorough tannage. When the goods are tanned they should be washed up in clean water and then allowed to drain for 12 hours. This recommendation is a very practical one and tanners generally agree that it improves the handle of the crust leather. The next operation is machine setting. After setting and just prior to hanging the skins up in the shed, it is advisable to smear over the grain a solution of sulphonated cod liver oil, one part of oil to five parts of water; taking care to give only a light smear. Drying is best carried out in an open shed under natural drying conditions.

When dry, the basils will need examining for greasy ones

which require degreasing in the petroleum degreasing plant. Next follows crust sorting and necking or backing on the shaving machine.

Dyeing and Finishing

Dyeing is fairly straightforward, using acid dyes where possible and aiming at good penetration of the grain. Very little fat-liquoring is necessary, but for heavy skins the addition of one-half per cent sulphonated cod liver oil on crust weight to the exhausted dye-bath is worth while. Washing up or rinsing, draining and setting-out follow in rotation, and after setting-out it is a good plan to smear over the grain a weak solution of glycerine, one part of glycerine to ten parts of water. Goods then need straining and drying in a fairly cool stove.

Finishing for printed goods is by no means complicated because, in the first instance, it must be kept simple to be economical. The leather first requires fluffing to get the flesh clean and the substance level. This is very important because really accurate printing is not possible unless the substance of the skin is uniform throughout. The presence of rough and irregular patches on the flesh side will lead to uneven embossing.

After fluffing, the goods should be lightly staked or stoned and then seasoned. Prior to seasoning it may be necessary to flame, top or lightly stain the grain so as to bring up the color and insure a really brilliant finish. The finisher usually tops by brushing on a weak solution of basic dye acidified with acetic acid. Instead of applying the stain by means of a brush, the writer considers that a more uniform and level result is obtained by spraying on the dye solution. This should preferably contain 5 per cent methylated spirits and 1 per cent gum tragacanth; the former to facilitate penetra-

tion of the dye and the latter to cover up defects, such as weak grain. Goods must then be aired off in a cool stove (not a hot one which will render the leather parched and lifeless) when they will be ready for seasoning. It is preferable to flame the goods than to use a colored seasoning. Before seasoning some tanners brush the grain to liven up the color and this is a sound practice.

Seasoning Recipe

A simple and economical seasoning may be made up as follows:

Soak ½ lb. 70–100 mesh casein and ½ lb. orange shellac in ½ gal. cold water for 12 hours. In a separate bucket dissolve 2½ ozs. ammonia (full strength) in ¼ gal. water. At the end of the period of soaking, heat up the casein and shellac solution to 120° F. and add the ammonia with constant stirring. Increase the temperature to 150° F. and add ½ oz. sulphonated castor oil. Boil and stir for 10 minutes. Allow to cool and settle for 12 hours and then add 2½ ozs. glycerine and dilute season to make 4 gals. Strain before use and add one-quarter of its volume of skimmed milk which tends to make the casein shellac film more elastic and adaptable.

According to Sutermeister and Browne in their recent book on "Casein," the advantages claimed for boiling the casein are that the solution remains undecomposed longer and is less subject to changes in viscosity on standing, which makes it possible to prepare successive solutions more uniformly. These authors recommend the addition of parachlormetacresol as a preservative likely to prevent decomposition of the casein solution.

After seasoning and airing off, the goods should be brushed, rolled, and printed, which is usually the final operation.

The method described in this article can, of course, be adapted to meet any particular requirements. Very few, if any, tanners cling to the same recipes and methods of working and their experience is that processes have to be worked out individually to suit their own special conditions of working and the plant available.

PROCESSING IMPORTED CRUST LEATHERS

In the case of imported crust leathers which have to be dyed and finished, the procedure recommended is somewhat different to that proposed for home tanned goods. After careful sorting comes shaving, if necessary, and trimming, the latter being very necessary as some Eastern skins, such as Bagdad sheep, have long necks and legs which are liable to cause knots during dyeing. The next operation should be wetting down and lightly stripping; water 100° F. and ½% washing soda on the weight of the goods for 15 minutes followed by a thorough washing in warm water 100° F. This stripping will remove a lot of filth and grease from the leather. Next, the goods require clearing with ¼% sulphuric acid on crust weight for 15 minutes, in cold water. After rinsing they can then be sumached with 5% sumach on the crust weight, or re-tanned with a mixture of myrobalans extract, quebracho, and chestnut. Afterwards the processing is practically the same as above.

BASILS FOR NATURAL SHOE LININGS

Lambs and thin sheepskins are the most suitable for this application. Although the general procedure can follow that explained above for basils to be printed, the writer considers it advisable to use a proportion of gambier in the tan liquor so as to obtain a somewhat softer leather. This is, however,

simply a personal preference and many tanners use a blended extract made up of myrobalans and quebracho (preferably sulphited).

Imported goods, such as Bagdad or Smyrna sheep and E. I. sheep, require well washing to remove excess of tanning material and lightly stripping, clearing, and re-tanning with about 2½ lbs. sumach to the dozen. To reduce the cost myrobalans and a little sumach extract may be used.

After re-tanning, the goods must be drained and then struck out, smeared over with a fatty mixture, such as can be made up by mixing ½ lb. sulphonated cod liver oil, ¼ lb. glycerine, 2 ozs. curd soap and ½ lb. colloidal clay in 5 gals. boiling water, mix well and cool to 65° F. before using. Allow skins to drain, then set them by hand or machine and strain. Home tanned crust goods should be given the same treatment. It is important where practical, not to dispense with the sumach re-tannage as this helps to lighten the color of the leather. In cases where the leather is dark in color it is a good idea to make use of a suitable synthetic tanning material recommended for bleaching purposes and there are a number of good proprietary products on the market.

Strained basils need trimming and fluffing then stoning and skating, followed by dusting with French chalk, rolling and brushing. These are often the only finishing operations required for a large proportion of goods. Instead of rolling, some tanners prefer plating, using a cold or slightly warm plate. The method of finishing must necessarily be very simple and economical, but a fair amount of latitude is given to the tanner in his choice of method.

At one time very large numbers of sheep for linings were tanned with cheap synthetic tanning materials of the Neradol type, but it was found that these did not stand up to wear as well as linings cut from vegetable tanned leathers; it was also brought to the notice of shoe factors that the shoes

were not as warm to the feet as the older type. These remarks refer to the cheap and strongly acid type of syntans, but there is no doubt that many of the modern products give excellent results, although, naturally, the best are too expensive for this type of tannage. When synthetic tanning materials are used for tanning, then it is advisable to re-tan the goods with sumach so as to add weight and give warmth to the leather. A method recommended by the writer is to add colloidal clay to the tanning liquor towards the last stages of processing. The fine particles of clay fill out a poor leather and also help very materially to improve the appearance of the crust leather.

For common white linings the easiest and quickest method is to use a synthetic tannage and finish off with a little sumach extract and clay, or when handling imported leathers to strip, wash, clear, and re-tan with a suitable synthetic tanning material.

XIII

DRESSING EAST INDIA SHEEP

East India Persians are popular with tanners specializing in leathers for fancy goods, bag, purse, and wallet work, etc.; also cheap bookbinding, shoe linings and slipper work, as well as meter diaphragms. There is good reason for the popularity of E. I. sheep for these purposes because the crust or undressed leather is very economical to finish and a wide range of tannages and qualities are available so that most requirements can be readily satisfied. In addition, the peculiar cross-bred nature and fine texture of the leather naturally lends itself to the production of high grade and attractively finished goods.

Most E. I. sheep and goat are tanned with turwar or cassia bark, which is indigenous to Southern India and contains 17 per cent of a catechol tannin. In many tanneries the turwar is blended with other cheap extracts to produce a leather not so liable to change color. In 1922 the author published some notes in *The Leather Trades Review*, London, on E. I. tannages, which may be worth recording.

In grading the various E. I. tannages, C. D. C., Pitty and N. B. are the palest and best, their only common defects being tick marks. The clear grained skins make very good plain colors, known in the trade as "smooths." C. D. C. are particularly spready and good pattern skins with not too much substance; they possess a clean flesh but are not so big

as Pitty or N. B. City tannages come next, of which Trichinopoly and Madras are the most important. These also are pale in color and are nice, square skins. Many of them are, however, heavily laden with sesame oil and lose one to two pounds per dozen when degreased. Light skins weighing six pounds per dozen have been found to lose as much as one pound. Coimbatoires are similar to City tannages but are not so spready as the latter and the skins have not such a regular and economical shape. Up-country tannages are darker in color than those mentioned and are usually very heavily laden with grease to the extent of as much as two to three pounds per dozen. Bangalores, Bombays, and Hyderabads are good examples of this class, being soft and spongy and only really suitable for blacks. The Dindigul tannage is easy to distinguish because of its peculiar yellowish color and is usually somewhat heavier than the City tannages. This extra weight is largely made up of grease and filling agents to the extent sometimes of 25 per cent of the total weight. Middle Town tannages, important examples of which are Vellores, Rashan and Nizan, are only suitable for blacks, linings and the stouter ones for embossing.

The crust warehouse should be lighted by means of a good north light. Common defects may be usefully catalogued as follows:

1. Dark color.
2. Irregular shape and uneven substance.
3. Tick marks, scab marks, scars, wasted grain, and rodent damage.
4. Butchers' cuts.
5. Badly nourished "fallen" skins.
6. Short hair or wool resulting from poor depilation.

For light colors, bleaches and self colors only the palest tannages can be used, the dark ones being relegated to blacks and dark colors, particularly printed goods. In many cases

the color can be greatly improved by degreasing, and where a petroleum degreasing plant is available and the price permits, then this method should be utilized. On the other hand, of course, stripping can be relied upon to remove a large proportion both of grease and excess tannage and considerable improvement can result from stripping and "souring" or acid clearing.

A large proportion of the heavier goods require necking, i.e., shaving down the neck, but for cheap lines this additional process has to be cut out and the goods merely cleaned up on the fluffing wheel. Shaving is, of course, a much more expensive and longer process than fluffing.

Stripping E. I. Sheep

There is some difference of opinion regarding the most suitable and efficacious method of stripping, but in the writer's opinion, choice of method should always be dictated by the nature of subsequent processes. If the maximum amount of grease, excess tannin and loading materials have to be removed, then washing soda should be employed, using about ¼ to ½ per cent by weight of ordinary soda at 85° F. After drumming goods in this weak alkaline solution for 20 minutes, the dark colored liquor should be run off and goods washed in running water for 20 minutes, followed by clearing in a solution of sulphuric acid, approximately ¼ per cent by weight, for 15 minutes, rising and draining ready for further processing.

On the other hand, if it is desired to dispense with acid clearing and so cut down cost of production to the absolute minimum, such as would be the case with cheap linings, slippers, children's footwear, etc., a less vigorous stripping action can be preferred, or in some cases, particularly blacks, it may be eliminated altogether. Borax or soap will remove

a useful proportion of grease and excess tannin without any corresponding darkening of the leather; about ¾ to one per cent of borax or textile chips (i.e., a good neutral curd soap). The temperature of the water should be not more than 90 ° F. and not less than 80° F. After stripping for 20 minutes, goods should be well washed in running water for 10 minutes, when they are ready for further processing. If no alkali is used, the temperature of the water should be increased to 95° F. and goods drummed for 30 minutes, followed by rinsing in cold water. For light, clear colors, "souring" or clearing is strongly advisable, also for bleached whites and naturals.

Sumaching

This process is strongly advisable as it improves both the feel and color of all goods which have to be dyed. About three to five per cent of sumach is necessary for good results. The procedure recommended is as follows: The required amount of sumach is thrown into the drum containing water at 90° F. and the drum run for five minutes. The addition of about ¼ pint of vitriol diluted to make one gallon of water should then be added to the drum and the goods put in ready for processing. About 20 to 35 minutes should prove sufficient, goods being washed up and stacked ready for dyeing.

It has been suggested that useful results may be obtained by substituting other and cheaper tannins for sumach, and while this can be done with fair results, nothing can really replace sumach. However, for dark browns and reds, etc., a mixture of gambier and sumach or cutch and gambier and myrobalans may be used; other useful retans are mangrove and chestnut, or, indeed, almost any clean working tannin able to replace that removed by stripping and to give the finished leather a full and well nourished handle.

Bleaching

Excellent results can be achieved by stripping with soda as described, washing, scouring in a dilute bath of sulphuric acid, and then drumming in a five per cent solution of a suitable bleaching synthetic tannin. There is no need to use any sumach, although if the goods are given a bath of sumach before processing in the syntan the color is improved. Bleaching by means of synthetic tannin will not give a dead white leather, but it will produce a very light colored one which can be readily pigmented and finished white. The writer recommends the following method for white E. I. sheep:

Drum in five per cent suitable bleaching grade of syntan for 30 minutes, temperature of solution approximately 75–80° F. At the end of that time run off half the spent liquor and add 2½ per cent colloidal china clay, 1½ per cent titanium oxide of dioxide, and ¼ per cent textile flakes. To prepare this mixture dissolve the soap in three gallons of boiling water and then stir in the pigment. Cool liquor by diluting with an equal quantity of cold water before adding to the drum. Process for 20 minutes, wash up in cold water and stack for several hours to drain. Strike out and strain. Dry in a cool stove. When dry, buff or fluff, then stake and finish. For cheap linings, socks, etc., all that may be necessary is to roll and iron the goods with a warm iron before measuring, but where a slight finish is required, this can be given quite economically by brushing on one coat of casein bound pigment dope and finishing off with two spray coats, the second one consisting mostly of binder or top finish. In the case of pastel tints it is necessary to color the goods with a small amount of acid dye after running in the syntan and to dispense with the pigment, although some tanners get

quite good results by adding a small portion of basic dye to the liquor containing the pigment. In this case it is advisable either to dispense with the use of soap or to add it last, about 10 minutes before the process ends.

An alternative method of bleaching which some tanners claim to give good results depends upon the use of barium chloride and sulphuric acid or sodium sulphate. The sumached goods are drummed in a five per cent solution of barium chloride (cold water) for 15 minutes, then transferred to a solution of one per cent sulphuric acid or 2½ per cent sodium sulphate and drummed for another 15 minutes so as to precipitate the barium salt as insoluble barium sulphate. Goods must be rinsed thoroughly after treatment and, if desired, they can be treated with a small amount of white pigment to finish off with. This method is much safer than the lead method and, moreover, the white barium sulphate precipitated on the leather is very stable and not so susceptible to atmospheric impurities as the lead salt.

Dyeing E. I. Sheep

As mentioned earlier, it is strongly advisable to sumach or otherwise retan all goods before dyeing, so as to insure full and even coloring. Acid dyes should be used (1½ per cent to two per cent); temperature of water, 95–100° F.; sulphuric acid equal in weight to the dye employed. The dye must be added in two portions, 10 minutes' difference between the first and second, and the acid added immediately after the second one. The addition of one per cent sulphonated oil, preferably a mixture of ½ per cent sulphonated castor, ½ per cent soluble mineral oil, may be added at the end of the dyeing process and drumming prolonged for 10 minutes. The use of even this small amount of fat-liquor

helps materially to improve the feel and general appearance of heavy goods, but if price of goods will not justify the extra cost, then it must be omitted.

Dyed E. I. sheep intended for bookbinding should be rinsed in a solution of ½ per cent sodium acetate after dyeing and allowed to remain horsed-up, draining, for six hours. They can then be struck out and strained. The type of finishing naturally depends on the character of the goods being manufactured. General procedure, however, for bag work is: take goods off the boards, damp them down, emboss and re-strain, then lightly stake, pad or brush, season on the table, air off, glaze or roll, re-season lightly, air off and re-glaze or roll, finally give a top spray, dry and plate or iron. Naturally methods vary a great deal, but as practically all E. I. sheep are for cheap lines, it is essential that operations should be cut down to an absolute minimum.

Velvet Sheep

For these it is necessary to choose skins with an unblemished flesh, the grain being of quite secondary consideration. After trimming and weighing the goods should be staked, fluffed and buffed, the latter being carried out with different grades of emery so as to get a very fine nap.

Goods should next be wetted down, stripped, rinsed, soured and sumached ready for dyeing. Approximately 2 to 2½ per cent acid dyes is necessary for best results; acid dyes being chosen because they are fast to rubbing.

One of the writer's actual recipes for red velvet sheep runs as follows:

880 grms. Acid Scarlet
5,000 ccs. Airedale Yellow
1,000 ccs. Formic Acid

This is for 10 doz. skins weighing approximately 75 lbs.

To secure good penetration and improve fastness of the dye, the writer recommends the addition of a small quantity of chrome liquor to the exhausted dye bath, approximately 1½ pints per doz. of a liquor of 99 basicity and 3 per cent chrome content. No fat liquor must be used.

After striking out, goods must be strained in a cool stove and when dry, weathered and staked, brushed on the machine and then lightly stoned to bring up the fine nap. Finally, the skins need ironing on the grain side with a warm iron and measuring ready for the finished warehouse.

Black Glazed Persians

These skins must be of a very good substance, large and spready. They are first shaved, that is, "necked" and "backed," scoured with a ½ per cent soda and then given a weak bath of sumach, about 2½ per cent at 85° F. When they are washed they are ready for dyeing, then they require rinsing in cold water, striking out and straining. They may then require topping with a solution of nigrosine, drying, seasoning, fluffing and re-seasoning and glazing. Finally they are oiled off with warm linseed oil, aired off and stored ready for measuring.

An old seasoning recipe which the writer's father passed down to him, and which has given excellent service, is as follows:

I

Take the whites of six eggs and beat up in one quart of blood. Now add one quart of milk and one of logwood—mix up together, beating up well.

II

Boil six ozs. of nigrosine crystals in a quart of water; when dissolved fill pail one quarter full of

cold water and mix I and II. Now add ¼ pint of Orchil, ¼ pint of wood naphtha and one sheet of French gelatine previously dissolved in boiling water which has been allowed to cool.

Meter Leather

East India Persians are generally used for meter leather and when properly selected and dressed they give every satisfaction. Skins most suitable for meter diaphragms should be chosen from good tannages, such as C.D.C., Pitty, and N.B., which give nice spready skins containing only moderate amounts of grease and other weight giving materials. Some of the City tannages are also quite useful, but care has to be taken with these so as to avoid heavily laden, spongy skins. The ideal leather for meters must be a smooth grained, pale tannage containing not more than ½ to ¾ lb. of oil and dressing per average dozen. In addition it must be free of tick marks and butchers' cuts, etc., which, even if they do not cause holes to appear in the leather, are a potential source of weakness likely to develop and become intensified under service conditions. Skins for meter leather should measure 30 inches from shoulder to butt and 18 inches in the narrowest part.

The sorter in the crust warehouse has a most responsible task, as it is upon his judgment that the quality of the meter leather largely depends. He must, therefore, be quick to recognize defects and to choose only those skins which he knows will give good service under the exacting conditions of wear in modern meters, especially if the gas contains a relatively high proportion of continuous vertical retort gas, which has a marked deleterious effect on the leather diaphragm owing to the high percentage of impurities which it contains.

To ensure that the crust sorter has the best possible chance of selecting the most suitable skins for the purpose, not only as regards size, but the less obvious but, nevertheless, equally important qualifications, it is a great advantage if he is given the opportunity of examining the goods in the brokers' warehouses and marking up the catalogs. Unfortunately the crust warehouse sorter is rarely given the opportunity of attending the sales and buying is frequently done either by the firm's special sales agent or a firm of outside brokers. The agent has not the highly specialized knowledge of the sorter and the outside broker cannot, or will not take the same amount of trouble as the tanner's own employe.

When the bales arrive from the sales they are broken up and goods carefully sorted for size and quality and very greasy skins picked out and sent to the petroleum degreasing plant. The meter goods are trimmed with hand shears, put up into dozens and weighed. They are next sent down to the wet shop for processing; the first operation being wetting down, preparatory to stripping and semi-chrome retanning. Wetting should be carried out by drumming the goods in warm water, 100° F., for 15 minutes. The use of wetting down agents is usually unnecessary, but if skins are inclined to be rather greasy and heavily loaded, then a small amount of wetting agent may be advantageously added to the wash water. Stripping should also be carried out in a drum, using approximately ¾ to 1 per cent borax (temperature of water 100° F.) on trimmed weight of goods. After stripping for 20 to 30 mniutes goods should be well washed in water at 95° F., drained or centrifuged to remove the bulk of water and then retanned.

The writer is of the opinion that semi-chrome retannage is preferable to any other as the resultant leather takes up more dressing than one that has been vegetable tanned, and the leather, even when the protective dressing is removed, has

a superior resistance to the corrosive action of moisture, sulphur and acids, tar residues and resinous compounds formed by the polymerization of the unsaturated hydorcarbons present in the gas.

A suitable chrome liquor for meter, and indeed most E. I. semi-chrome work, can be made up as follows:

36 lbs. potassium bichromate
30 lbs. sulphuric acid
18 lbs. glucose
21 lbs. salt
20 gallons water

Dissolve the bichromate in 10 gallons of the water raised to boiling point by means of a steam jet. Stir the liquor up well. Add the sulphuric acid very slowly pouring it through a sack to prevent splashing. Stir the liquor thoroughly then add the glucose dissolved in three gallons of boiling water. Agitate the liquor, then boil for 10 to 20 minutes. Make up to 20 gallons of liquor.

Approximately seven gallons of the above liquor per 100 lbs. of crust goods will give good results. After retanning for at least two hours, goods should be horsed up for two hours, washed, neutralized with borax approximately 1 to 1½ per cent, washed thoroughly, struck out and strained, staked and buffed, brushed and ironed. It should be pointed out that the large bulk of meter leather produced in Great Britain is merely shaved, cleared with sulphuric acid, one pint for 100 skins at 85° F., strained, staked, buffed, brushed and ironed. The method recommended by the author will, however, produce a very superior type of meter leather, but it is problematic if the meter manufacturer will pay the price, even if he is told of the extra life of the leather.

The leather is usually sent to the meter manufacturer, who cuts out the diaphragms and treats the leather to preserve its life by rendering it immune to the action of the

corrosive elements present in the gas. The anti-corrosive treatment generally consists of an oleaginous mixture made up of equal parts of whale oil and neatsfoot oil and a small proportion of paraffin wax. Afterwards the leather is varnished, lacquered or otherwise protected. The writer considers that the latest dispersion of acrylic and styrene resins should prove of the greatest value to manufacturers looking for a highly flexible and yet water resisting finish for meter diaphragms.

Crust Goods for Semi-Chrome Clothing and Gloving Leathers

In the writer's opinion the best results are obtained by chroming crust leathers rather than taking vegetable tanned goods direct from the tanhouse. In the latter case the finished goods are inclined to be pipey and loose and the grain is more uneven and drawn, all of which characteristics are definitely damaging to the quality of the leather. Although it may appear to be waste of time, material and labor to take the trouble of drying the leather after vegetable tannage, it is very definitely worthwhile if the best results are to be obtained.

If, however, it is not possible to dry out the goods after the first tannage, then they should be well drained, struck out and allowed to sam on horses for 36 hours before retanning and in this case the vegetable tanning process should be so adapted that the goods are slightly undertanned so that no stripping is necessary, only a brief wash in warm water. Alum tanned goods also react beneficially to drying as this helps to fix the complex aluminum protein groups and render the tannage permanent. If goods are taken straight from the alum for chroming there is a decided tendency for the finished leather to be somewhat tinny and lacking that full,

flexible handle so desirable in the case of good quality clothing and gloving. On the whole, the author is of the firm opinion that it pays to go the long way round. Possibly this view is old fashioned, but the "old 'uns" certainly did "know their stuff"!

Choice of vegetable tanning materials for the first tannage is important as experience has shown that not all tanned goods react in the same way when chromed. An inexpensive blend of myrobalans and quebracho or myrobalans and hemlock gives excellent results and is a good deal better than blends containing chestnut or oakwood. A quick and satisfactory preliminary tannage may be achieved by the use of alum and gambier, the only disadvantage of this mixture being that it is liable to accentuate any tendency of the goods to be loose or fluffy.

Stripping

Vegetable tanned goods require stripping before retanning, in order to remove excess of tanning matters and prepare the fibres for the chrome content. Various stripping agents are available, but one of the best and simplest is soda ash 1–1½%, the amount depending on the condition of the goods. Usually home tanned skins do not require more than 1% and imported crust about 1½–2%. Some of the eastern skins are very dirty and they should be well washed in warm water, 120° F., for 20 minutes before stripping, the latter operation being carried out in a drum.

To insure absolute uniformity of results it is advisable to measure out the volume of water used, about 300% on the dry crust weight being a good working figure. In the case of alum leathers the use of alkali is unnecessary as drumming in warm water will remove all the uncombined salts that is required. Drumming in 300% warm water, 125° F., for 15 minutes is recommended.

After stripping, the goods require a thorough washing in two changes of warm water, 40° F., each change taking a minimum of 10 minutes. This washing is absolutely essential in order to remove all traces of the alkali-tannin substances and to leave the grain of the leather clean and in a condition to take on a good color when chromed. If washing is omitted or seriously curtailed there is a risk of the leather being stained and these stains may show up if the goods are to be finished in light colors.

Retanning with Chrome Liquors

For the actual chroming it is possible to use one of three different preparations; first, a home made liquor produced by reducing chromic acid with glucose, etc.; second, a solution of ammonia chrome alum, and third, a proprietary chrome liquor containing a standard chrome content and specified basicity. All three liquors can, in capable hands, give excellent results, but for general convenience the use of a first class proprietary chrome liquor or powder is recommended. The general run of these have a chrome content of 15–27% Cr_2O_3 and basicity (Proctor) ranging from 144–88 (the high chrome content represents a powder compound). For the best semi-chrome tannage a basicity of 96 is recommended and a batch liquor of 15% Cr_2O_3, using 10% on the crust weight. In the case of ammonia chrome alum, the basicity of which is generally 144, the addition of 11.07% soda ash on the weight of alum is necessary to give a basicity of 96, the alkali dissolved in a small quantity of water being added to the solution of chrome alum very slowly and with constant stirring.

A really good chrome liquor can be made up as follows:

36 lbs. potassium bichromate
30 lbs. sulphuric acid

18 lbs. glucose
21 lbs. salt
20 gals. water

Dissolve the bichromate in 10 gals. of water raised to boiling by means of a steam jet. Stir the liquor up well. Add the sulphuric acid very slowly, pouring it through a sack to prevent splashing. Stir the liquid thoroughly, then add the glucose dissolved in three gals. of boiling water. Agitate the liquor, then boil for 10–20 minutes and finally make up with cold water to 20 gals. of liquor. The salt may be added in the case of pickled goods, but omitted for tanned leathers (that is goods for semi-chrome). It is, however, a good practice to add a few pounds to the semi-chrome liquor.

This recipe is recommended as a general purpose formula suitable both for direct tanning of pickled goods and all kinds of semi-chrome goods.

Retannage should be carried out in a drum using 250% water on crust weight. For average weight basils, about three hours' tannage is usually sufficient. The chrome solution should be divided into six portions and a portion added to the liquor every 30 minutes. When the tannage is complete a cutting from the neck or butt should be taken and boiled for three minutes, the boiled sample being afterwards examined to discover shrinkage which should not exceed 15% (this is generous as most tanners insist on 12%). The writer must admit some doubts about the benefits of the boiling test as he has seen chromed leather which would not stand up to boiling and yet proved to be exceptionally hard wearing and serviceable. Although a high chrome content may be desirable it is by no means essential and good clothing leather may contain as little as 1–1.5% Cr_2O_3. After tanning the goods should be horsed up and allowed to drain for 24 hours, afterwards struck out, necked or lightly shaved, weighed and then washed and neutralized.

Neutralizing

Although some tanners omit this process in the case of semi-chrome goods, strange to relate the author has not noticed any difference in the appearance or handle of the goods when neutralization is omitted. Indeed, excellent results may be achieved by merely washing the goods. The full neutralization process is, however, given below for those who wish to carry it out in full.

Bicarbonate of soda is recommended for neutralizing, using 0.25% on the damp shaved weight. Washing in several changes of cold water should precede neutralizing, which is best carried out with 300% water for 20 minutes or until the surface of the leather is only faintly acid, preferably pH 5. Although most tanners still use litmus papers which are very convenient and give reasonably accurate results, the use of more accurate indicators is recommended, preferably Brom-Cresol purple. After neutralization the goods require washing in running water, using the lattice door of the drum, for 20 minutes. They can then be drained overnight and dyed next morning.

Dyeing

Unless the chrome content of the leather is high there is no need to mordant the goods as most effects can be obtained by the use of acid dyes using a higher temperature than would be the case with pure vegetable tanned basils.

From the author's notebook comes the following recipe for dyeing semi-chrome goods.

"Make up drum with warm water, 125° F., using 250% water on shaved weight, then add ½% formic acid on shaved weight. Run goods for four minutes and then add

1% Airedale Yellow and continue processing for a further five minutes. Add the dye formula dissolved in two gallons of boiling water (cooled to 120° F. before adding). After 10 minutes add a further ½% formic acid and run goods for 40 minutes."

SORTING E. I. PERSIANS IN THE CRUST WAREHOUSE . . .

FAT-LIQUORING

Fat-liquoring can be carried out with one of the proprietary fat-liquors or a straight emulsion of sulphonated cod-liver oil, using 4% on shaved weight. Fat-liquoring can be carried out in the spent dye liquor provided the temperature of the liquor has not fallen below 100° F. Run goods for 40 minutes, then take out of liquor and allow to sam for at least four hours or so before striking out and setting by machine. Hang in cool shed to dry.

Finishing

Season with damp sawdust, stake out on a suitable machine and then buff. Spray or dope on the table with a pad. Hang up to dry, spray with top finish, dry off, stone, brush and roll ready for measuring. The writer advises the use of a casein bound pigment for the ground coating and then finishing off with a clear cellulose lacquer able to give a water resisting flexible coating. The use of a suitable dope for topping off semi-chrome is far better than the usual fastening coating, but it must be admitted that a good deal of care is still necessary in the choice of a cellulose spray for this purpose.

The danger in purchasing cheap lacquers is that the least expensive plasticizers will be used by the manufacturer and to obviate this some of the more particular tanners are now adapting standard lacquers to meet their own requirements. The use of complex cyclo hexanyl adipates and their homologues is receiving attention. Dimethyl cyclohexyl ester of adipic (Sipalin A.O.M.); methyl cyclohexyl ester of methyl adipic acid (Sipalin M.O.M.) and dicyclohexyl ester of adipic acid (Sipalin A.O.C.) manufactured by the Deutsche Hydrierwerke A.G. can be used in conjunction with castor oil to give improved finishes. Another Sipalin is the Sipalin Special which is a mixture of the dimethyl cyclohexyl ester of methyl adipic acid with palmitic acid ester.

Semi-Chrome Persians

Semi-chrome gloving E.I. sheep should be nice quality skins and fairly stout in substance. They are first stripped with 1½% washing soda, well washed and then given a bath of glucose reduced chrome liquor, basicity 96, using suf-

ficient chrome to give 1–2% Cr_2O_3 content in the finished leather. After chroming they are well washed in cold water, slightly cleared, then dyed with acid dyes and washed, struck out and hung up to dry, staked and buffed or they may be buffed in the crust condition. They are then doped and dried, ironed and finished. The slight clearing is carried out with ⅛% sulphuric acid on the crust weight and is recommended by tanners specializing in this class of work who insist that, contrary to all theory, a better leather is produced and certainly deeper penetration of dye secured.

In the case of greasy E.I. sheep or goat, when it is not convenient to put them through a proper degreasing plant they can beneficially be treated with a solvent soap instead of washing soda or soda ash. One of the best soaps for this purpose contains cyclohexanol.

Drying Semi-Chrome Goods Before Dyeing

It is sometimes convenient to dry goods after retanning and before dyeing and this may be carried out quite easily. One of the earliest and best known methods is mentioned by Flemming in his book "Practical Tanning." He recommends drumming 100 lbs. of shaved goods in 12 to 15 gallons of water containing 3 lbs. lactic acid for 10 minutes, afterwards draining the leather and drying in the usual way. He mentions that goods treated in this way may be stored away until it is desired to finish it, when it can be wet back with water, colored, fat-liquored, and finished. The wet skins, after the acid bath, can be tacked out on boards to dry, which enable the tanner to get the greatest possible measurement.

Recognized wetting agents of the sulphonated higher alcohol or sulphonated aliphatic ester are now used to a considerable extent, both before drying out and when wet-

ting back the crusted leather. The author strongly recommends this double procedure for the best results, as it saves a good deal of worry when crust goods do not soak back readily. There are literally dozens of excellent proprietary wetting back agents on the market. The writer has found that a very satisfactory procedure is to fat liquor the goods with a special mixture containing cyclohexanol which possesses remarkable solvent, wetting-out and emulsion stabilizing properties. The mild camphoraceous odor of this solvent is not noticeable in the finished leather. The use of a fat liquor made up of sulphonated castor, sulphonated codliver, soap and cyclohexanol or methyl-cyclohexanol is very satisfactory if prepared in the following way. Best textile flakes are dissolved in a little boiling water and the sulphonated oils added with constant stirring. When the solution has cooled down to 130° F. the solvent should be added very slowly.

A recipe worked out on the following lines is suggested.

½% textile flakes on damp shaved weight.
3% sulphonated oils (85% cod and 15% castor).
2% cyclohexanol.

When wetting back the goods for fat-liquoring, a little cyclohexanol soap mixture will assist the process. Although it is not claimed that this process is as efficient as some of the proprietary wetting back agents, the latter are very expensive and in some cases produce a rather flat and lifeless handle in the finished leather.

XIV

CHROME TANNED SHEEPSKINS FOR CLOTHING AND LININGS

FELLMONGERED pelts suitable for full chrome must be first quality skins with a perfectly sound and clean grain, of medium or heavy weight and good square shape. Thin, poor pelts are quite unsuitable for chrome tanning, which adds very little actual weight to the leather and therefore cannot be trusted to build up the pelt in the same way as vegetable tanning. English tanners deal with three types of full chrome goods: lambs, linings, and motors.

LIMING

After fellmongering the goods must be limed in a weak sulphide lime made up with slaked lime and sodium sulphide to give a total alkalinity of 7–9, depending on the type of pelt being processed. Drums, paddles and pits can be used. The most suitable drum for general beamhouse work is made of oak, about 10 ft. in diameter, and revolving at one complete revolution per minute but able to be speeded up to four revs. per minute when used for washing. Paddles of a capacity of 1,000 gallons are very convenient. The author prefers brick lined pits for liming, but he is, of course, aware that excellent results are being obtained by use of both drums and paddles.

Drum liming can be completed in about 36 hours, running

the drum for a period of 15 minutes every four hours. Paddle liming should be continued for 48 hours, running the wheel for 20 minutes at a time every six hours. Pit liming requires three days, giving the goods at least six draws throughout the period and taking care that the liquor is well plunged up before throwing back the goods.

Deliming

When properly limed the goods must be pieced or trimmed, then fleshed, cobbed (loose wool removed) and finally scudded by hand or machine. Before scudding the goods should be soaked for a few minutes in water at 85° F., which softens them and gets them in the correct condition for scudding, the aim of which is to remove all the fine wool fibres and also pigment and fat. Unless scudding is properly carried out there is a grave risk of the grain being clogged and dirty and showing to great disadvantage in the finished leather, especially in the case of light colored leathers.

When scudded the goods can be washed in the drum in running cold water, employing the lattice drum. Washing for 15 minutes renders the pelts in suitable condition for deliming. If desired, washing can be carried out in the paddle. For a paddle of 1,000 gallons, two quarts of hydrochloric acid or one quart of formic acid will be necessary, the acid being diluted before adding to the contents of the paddle. Usually about 30–45 minutes will be found sufficient to render the cut surface just faintly alkaline to phenolphthalein. Provided the goods are not rendered acid by deliming, they can be passed straight away into the puer or bate.

Puering or Bating

To prevent loss of valuable skin substance this process must not be exhaustive in its action. Puering can be carried

out in either drum or paddle, preferably the latter. For 100 lbs. pelt about 1½ lbs. enzyme bate is sufficient, the solution being maintained at 98–100° F. Half an hour is long enough to produce the desired degree of puering.

Washing and Pickling

A few minutes in cold running water is sufficient to prepare goods for the pickle. The latter should be equivalent to a decinormal solution of hydrochloric acid and 10° Twaddle salt, running the paddle for 1¼ hours.

Chrome Tanning

The best clothing leathers are tanned by the two bath process, which produces the softest leather and one ideally fitted for clothing purposes. Drums are generally used for tanning and a very convenient size is one holding about 30 cwt. goods and 90 cwt. liquor, revolving at 6–8 revolutions per minute. The drums should be fitted with shelves instead of pegs which are liable to knot the skins, especially if they have not been properly trimmed. Knotting can be very serious and the author has known a huge ball to be formed made up of five or six dozen skins, which may be so badly marked as to be suitable only for blacks.

American pitchpine is a splendid wood for chrome tanning drums and most tanners prefer it even to larchwood, which is considered very hardwearing. All tanning drums should be provided with well fitting doors, preferably fitted with pressure screws which will enable the doors to be closed both quickly and tightly. An excellent idea is to have all exposed metal fittings treated with a suitable phenolic coating which will protect them against the corrosive effect of acids, including chromic acid. The Lithcote process entails the treatment

of the metal with a proper phenolic resin in a solvent, drying of the resin and curing at a scientifically controlled temperature for a calculated length of time.

The First Bath (Yellowing)

The laps of pickled goods should be opened out, individual skins well shaken and thrown into the tanning drum used for yellows. The contents recommended are as follows:

800 lbs. pelt

Salt 50 lbs. Hydrochloric acid 1 gal. Water 45 gals.	110° F. 30 min.

At the end of 30 minutes the chromic acid solution, made of as follows, should be added.

Bichromate of soda 58 lbs. Hydrochloric acid $2\frac{1}{4}$ gals.	90° F. 2 hours

Dissolved in 5 gals. warm water 100° F.

The chomic acid solution should be added slowly through the hollow axle, taking at least 10 minutes over the addition.

An alternative method is to run the pickled goods in brine made up of:

800 lbs. pelt

Salt 35 lbs. Water 65 gals.	100° F. 30 min.

At the end of the given time the chromic acid solution containing the full amount of hydrochloric acid should be added.

Bichromate of soda 48 lbs. Hydrochloric acid 36 lbs. Salt 8 lbs.	3 hours

Dissolved in absolute minimum of water.

Practical recipes for two bath tannages are exceedingly numerous and every tanner has his own favorite method; some do not favor the presence of a neutral salt in the yel-

low and others prefer the use of sulphuric acid instead of hydrochloric. The original Schultz recipe did not include salt.

5 lbs. Bichromate of potash 2½ lbs. Hydrochloric acid	} per 100 lbs. pelt

The above is still used and apparently gives very satisfactory results. M. C. Lamb says that the presence of the large amount of undecomposed potassium bichromate is useful as it averts the liability of damage by an excess of acid and also influences, beneficially, the rate of absorption of chromic acid. Lamb points out, however, that any neutral salt will achieve the same ends, it being much more economical to use sufficient acid to affect the conversion into chromic acid and to add to the solution an excess of a suitable neutral salt.

There is no difference in the working properties of potassium or sodium bichromate, but the latter is a good deal easier to dissolve. Red triclinic and monoclinic crystals of potassium bichromate dissolve at the rate of 4.65 parts in 100 parts of cold water and 102.0 parts in 100 parts of boiling water. Red triclinic crystals of the sodium salt dissolve at the rate of 239 parts per 100 parts cold water and 1,226 parts per 100 of boiling water. The sodium salt is cheaper than the potassium salt, but against its improved solubility is the fact that it is hygroscopic and therefore liable to become moist when stored in a damp place. In view of this the precaution should be taken of either storing the kegs in a dry storeroom or buying strictly up to demands and carrying very little stock.

The optimum time to be allowed for goods in the yellow may vary from 2–4 hours and it is impossible to lay down any hard and fast rule. Excellent results can, by using certain formulae, be obtained by drumming only two hours; on the other hand a somewhat different recipe may require the

full four hours for the best results. It will be noticed that the two recipes given require periods from 2–3 hours. The aim of the tanner is to secure thorough penetration of the skins with the chromic acid solution. The writer prefers the use of the absolute minimum of liquor and the first recipe given can be thoroughly recommended as representing the very best British practice.

Reducing

When thoroughly yellowed the goods should be allowed to drain on horses for 12 hours, taking care that the skins are smoothed out on horses so that no creases are present. If the goods are just thrown carelessly onto the horses and this point is not watched, then it may prove difficult to remove the creases when the goods are set. Next morning the goods should be struck out, avoiding the use of too much pressure otherwise chromic acid will be squeezed out to the detriment of the leather and cause it to be flat and tinny. After striking out, the pack can then be reduced either in the drum or paddle, preferably the latter. For a pack of 800 lbs. pelt the following proportions are recommended:

Sodium thiosulphate 110 lbs.
Hydrochloric acid 1 gal.

The hypo should be dissolved in hot water (solubility of this salt is 110 parts in 100 parts of cold water and 301.5 parts in 100 parts boiling water) and added to the water of the paddle before putting in the goods. The acid can then be emptied in and liquor stirred up well before working. Temperature of solution at the time goods are thrown in should be 94° F. After five minutes' running a further quantity of acid should be added.

Hydrochloric acid 4 gals.
Water 2½ gals.

At the end of one hour add

Sodium thiosulphate 50 lbs.
Hydrochloric acid 2 gals.
Water 2½ gals.

Run for a further hour and then add 20 lbs. hypo and ½ gal. acid in 1 gal. water and continue processing for 2 hours.

Reduction in the drum can be carried out as follows: For a pack of 800 lbs. pickled pelt run in 130 gals. water at 100° F., add 100 lbs. hypo and 5 lbs. hydrochloric acid diluted with a little water. Run drum for a few minutes and then throw in goods and start up drum. At the end of five minutes add 15 lbs. of acid diluted with three gallons of water. In 45 minutes' time add 30 lbs. hydrochloric acid and 10 lbs. hypo dissolved in six gallons water. Run for ½ hour and then add the remainder of the acid and hypo, namely 10 lbs. hydrochloric acid and 15 lbs. hypo in five gallons of water. Process for a further hour and a half.

Washing

When reduction is complete and a cutting from the neck or butt has been proved to stand up to boiling for three minutes without serious shrinkage, then the goods should be drained for eight hours on horses or trays and then washed in running water (cold) for 3½ hours. It is better to wash goods in a drum with a lattice door than in a paddle. Next morning the pack must be neutralized, although some tanners maintain that this is not absolutely necessary for two-bath tannages and that a further drumming in warm water, 100° F., is quite sufficient.

Famous English Tanner's Chrome Tanning Recipe

A well known English tanner specializing in high grade chrome clothing leather uses the following formula.

For a pack of 20 doz. linings, or 12½ doz. motors. Drum in salt and water made up with

33 lbs. common salt.
36 gals. water.

Run for 20 minutes and then add 33 lbs. sodium bichromate. First of all make up 30 gallons of chrome in a wooden tub by dissolving the 33 lbs. of bichromate and 2½ gallons hydrochloric acid. Take 15 minutes to run on this liquor. Run 2½ hours in the yellow. Horse up all night and see that the skins are properly covered up during the period of standing.

Reduce next morning. Dissolve a little hypo in water in drum to start with, approx. 5 lbs. Then when drum has started up add 63 lbs. hypo and five gallons hydrochloric acid. Reduce for 5 hours. Wash in warm water, 90° F., for one hour and then neutralize with 16 lbs. borax for ¾ hour. Wash one hour and then dye straight away.

NEUTRALIZING

Drumming in a 0.25 to 0.5% sodium bicarbonate or 1.5% sodium phosphate (on 100 lbs. of pickled pelt) at 85° F. is usually sufficient to achieve the correct degree of neutrality, surface sufficient acidity pH5. The volume of water should not exceed 250%. Excellent results can also be obtained by use of 1.5% borax. Time required for neutralization naturally varies somewhat according to the type of alkali employed. Thus for bicarbonate 20 minutes should be regarded as the maximum time to be allowed; ½ hour for sodium phosphate and ¾ hour for borax. Various claims are made for these several alkalies, but the writer has never been able to detect any difference in the finished leather when a change is made in the alkali used. It is, of course, a fact that more care has to be taken when employing some alkalies than others; borax is a very safe alkali and bicarbonate is also

reasonably safe. Tanners who have tried out sodium metaphosphate report that it is very satisfactory, but it is, of course, a relatively expensive chemical and bumps up the cost of processing. After neutralizing a second washing for one hour in running water at 95° F. is necessary to remove all the soluble salts. Drain, set and shave ready for dyeing.

Dyeing

Immediately before dyeing the pack should be washed up in water at 110° F. for 10 minutes and then transferred to the dye drum. There are at least four methods of dyeing chrome; dyeing with acid dyes; combination of acid and basic; basic; direct colors (usually reserved for blacks). The writer considers that a combination of acid and basic dyes gives the best result for clothing leathers and the method recommended is as follows:

Drum the pack in a mordanting solution made up of

1½% tannin (percentages on 100 lbs. shaved moist leather).
250% water at 110° F.

The nature of the mordant must naturally be left to the discretion of the tanner, but for blacks there is nothing better than hematine crystals; dark browns, hemlock extract or gambier; light colors, sumach extract. Usually ½ hour to ¾ hour is sufficient to secure sufficient penetration. Although dyeing can be carried out in the same drum as the mordanting, it is recommended to use a different drum. As mentioned in previous installments, it is of little practical importance to give actual recipes for dyeing without providing a color chart: it is, however, a valuable guidance to provide general working directions which can be easily adapted to the tanner's own particular requirements.

Dyeing is best carried out in a drum containing ultimately

½ the quantity of dye (1½–8 oz. per cent)
1½ oz. per cent ammonia
250% water 130° F.

At the end of 10 minutes add the remainder of the dye dissolved in boiling water which has been cooled to 140° F. Sieve before pouring through the funnel. In 10 minutes' time add the acid

1% formic acid diluted with 10 times its volume of water.

Run drum for a further 15 minutes, when the color should be fixed.

Topping with basic colors can now follow in the exhausted dyebath using approximately two oz. per cent of dye dissolved in twice its weight of 30% acetic acid. Continue dyeing for 30 minutes, and then fat-liquor.

This method of dyeing is naturally somewhat lengthy and expensive and in some cases the topping may be omitted, using twice the quantity of acid dye and prolonging dyeing for a further 15 minutes. In this latter case it is advisable to fat-liquor before dyeing as acid dyes are not so resistant to alkalies as basic colors. Straight dyeing with basic dyes can give excellent results and the following method is recommended. Drum with the selected tannin using

1½-2% extract depending on the shade required
300% water at 135° F.

At the end of 25 minutes add 1¾% tartar emetic and continue drumming for 15 minutes. Add the basic dye about 4–8 oz. per cent (100 lbs. shaved leather) dissolved in weak acetic acid and run for 30 minutes. Fat-liquor in the same liquor.

Direct or chrome colors, particularly black, can be used, but they do not generally give such a high degree of penetration as is possible by the use of acid or basic colors, or a combination of both. Goods should preferably be lightly

mordanted with ½% fustic and then dyed with 5–9 oz. per cent of dye; larger quantities of dye being necessary in this case. Temperature of liquor should be 140° C. and the goods run for 25 minutes when fat liquoring can be carried out

FLOW SHEET FOR 800 LBS. PICKLED SHEEP
(Pickling-Fat-Liquoring)

Process	Vessel Used	Revs. per Min.	Time	Temp.	Recipe
Yellowing	Drum	7	2½ hrs.	110° F.	Salt 50 lbs., hydrochloric acid 1 gal., water 45 gals.—First period ½ hr. Bichromate of soda 58 lbs., hydrochloric acid 2¼ gals., water 5 gals.—Second period 2 hrs. Temp. 98° F.
Reducing	Drum	7	3 hrs.	100° F.	100 lbs. hypo, 5 lbs. hydrochloric acid, 130 gals. water —5 min. 15 lbs. hydrochloric acid, 2 gals. water—45 min. 30 lbs. hydrochloric acid, 10 lbs. hypo, 6 gals. water—30 min. 10 lbs. hydrochloric acid, 15 lbs. hypo, 5 gals. water—1 hr. 30 min.
Washing	Drum	7	3½ hrs.	45° F.	
Neutralizing	Drum	7	20 min.	85° F.	3½ lbs. sodium bicarbonate, 200 gals. water.
Washing	Drum	7	1 hr.	95° F.	
Dyeing	Drum	7	35 min.	140° F.	Mordant with 10 lbs. tannin and 200 gals. water. Dye with 4½ lbs. acid dye and 1 lb. ammonia. Fix with 8 lbs. formic acid.
Fat-liquoring	Drum	7	30 min.	95–110° F.	8 lbs. sulphonated cod liver oil, 12 lbs. sulphonated castor oil, 4 lbs. textile soap flakes, 2 lbs. mineral oil—Thoroughly emulsified.

FLOW SHEET FOR 800 LBS. PULLED SHEEP
Liming-Pickling (Drum Working)

Process	Vessel Used	Revs. per Min.	Time	Temp.	Recipe
Liming	Drum	1	36 hrs. Drumming 15 min. ev. 4 hrs.	45° F.	6 lbs. sodium sulphide 25 lbs. hydrated lime 250 gals. water
Washing	Drum	4	10 min.	45° F.	
Deliming	Drum	1	20 min.	45° F.	6 lbs. formic acid 250 gals. water.
Puering	Drum	1	25 min.	98° F.	12 lbs. pancreatic bate 200 gals. water.
Washing	Drum	4	10 min.		
Pickling	Drum	1	20 min.	45° F.	Decinormal hydrochloric acid and 10° Twaddle brine.

Fat-Liquoring

Excellent results can be obtained by the use of some of the proprietary fat liquors, but these are generally more expensive than home made preparations. A good fat liquor for chrome sheep may be made up as follows:

Sulphonated codliver oil	1 %
Sulphonated castor oil	1½%
Textile soap	½%
Mineral oil	¼%

The whole of the oil and soap should be dissolved in 5 gallons of boiling water and then thoroughly emulsified for 10 minutes. An alternative recipe is

Sulphonated castor oil	1 %
Castor oil	½%
Castor oil soap	½%
Eggyolk	½%

When using the latter fat liquor, the precaution must be taken to see that the temperature of 95° F. is not exceeded either for making up the liquor or using it in the drum.

The author considers that castor oil, either neat or sulphonated, should always be present in the ideal chrome fat liquor. Fat-liquoring should be continued for 30 minutes.

FLOW SHEET FOR 800 LBS. PULLED SHEEP
Liming-Pickling (Paddle Working)

Process	Vessel Used	Time	Temp.	Recipe
Liming	Pit	3 days	35° F.	Total alkalinity 8. Liquor made up of slaked lime and sodium sulphide.
Washing	Paddle 1,500 gal. cap.	30 min.	35° F.	
Deliming	Paddle 1,000 gal. cap.	30 min.	35° F.	½ gallon commercial hydrochloric acid added in three portions (diluted). Process completed when cut surface of heavy skin just pink with phenolphthalein.
Puering	Paddle 750 gal. cap.	30 min.	98° F.	10-12 lbs. of suitable enzyme bate.
Washing	Paddle 1,500 gal. cap.	10 min.	98° F.	
Pickling	Paddle 750 gal. cap.	1¼ hrs.	35° F.	Decinormal solution of hydrochloric acid: Brine 10° Twaddle.

After fatliquoring, the goods must be taken out of the drum, drained and then struck out and set ready for drying. It is advisable to allow several hours to pass between draining and setting so as to enable the fatliquor to be thoroughly absorbed by the fibres. Skins need to be hung up on poles in a warm stove 85° F, where there is a good current of warm air circulating. When dry the goods must be taken down, dampened in clean pine sawdust and when properly conditioned staked and immediately strained ready for finishing. Straining should be carried out at 90° F.

Finishing

Some tanners clear the goods with a weak solution of lactic acid, 10 per cent strength, which helps to remove the surface grease. Very greasy skins require solvent degreasing and some tanners carry this out as a matter of course as

they consider that the complete removal of grease removes one of the hazards of finishing, especially when cellulose dopes are used. On the other hand, some tanners manage to dispense with degreasing by wiping the grain of the leather with a sponge saturated in a suitable solvent, preferably one of the chorinated solvents.

The whole aim of the finisher should be to preserve the genuine handle and appearance of the leather and for this reason the minimum amount of finish must be used.

A suitable finish for the priming coat is the following:

Pigment finish	10 parts	Thoroughly mixed by means of an emulsifier
Casein solution 10 per cent	10 parts	
Shellac solution 10 per cent	10 parts	
Sulphonated caster oil	1 part	
Glycerine	½ part	
Water	50 parts	

The goods should be padded with the finish using the minimum quantity and then dried at 85° F. They then require staking or stoning and then fluffing. Afterwards they should be given a light spray of finish and when aired off sprayed with either a suitable water-resistant lacquer or a coagulating mixture made up of

Formaldehyde	10 parts
Acetic acid	½ part
Water	30 parts

The use of a suitable nitro-cellulose lacquer is preferable and many tanners now definitely prefer one specially adapted to their requirements and able to give a semimat or mat finish. When properly dried the goods need well brushing and warm plating ready for measuring.

It is not possible to over emphasize the fact that the finishing must be designed to give an exceptionally smooth and natural appearance to the leather.

White Chrome Sheep

Only the finest quality pelts should be chosen for whites and while the general instructions given for ordinary chrome sheep apply, extra care must be taken during the scudding. The recommended practice is to scud before and after puering so as to remove the maximum amount of pigment. The extra expense involved in duplicating this operation is well worth while.

After pickling it is advisable to examine the goods and to throw out any skins showing stains, heavy pigment deposits and other serious defects likely to render the pack unsuitable for whites.

Neutralize the shaved goods with one per cent borax at 95° F. for 20 minutes. Wash in warm water, 100° F., for ¾ hour and then clear with ½ per cent sulphuric acid for 15 minutes; follow by a thorough washing in warm water 95° F. The goods are now ready for bleaching with a suitable synthetic tanning material. Drum in a 10–15 per cent tanning solution at 120° F. for one hout, drain and wash in several changes of warm water, 120° F., for 1½ hours. Now pigment the leather with the following mixture:

5 per cent Colloidal clay 3 per cent Titanium oxide 2 per cent Lithopone 1½ per cent Flour 200 per cent Water, 100° F.	Percentages on shaved weight

An alternative recipe is the following:

Drum the goods in the following solution:

3½ per cent Barium chloride
150 per cent Water at 110° F.

After 15 minutes add the following:

4 per cent Glaubers Salt dissolved in 5 gallons

water 120° F. Drum for 25 minutes, then add 3 per cent titanium oxide and continue for another ½ hour.

Fatliquoring can be carried out in the pigment solution or a separate solution. The writer considers that it is preferable to add the fatliquor to the exhausted pigment bath, using about three per cent mixed sulphonated acids; a mixture of sulphonated cod and castor oil works extremely well.

After fatliquoring allow goods to drain for 12 hours, then strike out and set. Hang on poles to dry in a warm stove; damp down in perfectly clean pine sawdust, stake and strain. Degrease, if necessary, and then finish. Pad with a minimum amount of white pigment finish, dry off, stake and fluff, then spray top coat, air off and plate warm. Very little finishing of any kind should be necessary if the goods are properly processed.

Careful selection of the synthetic tannin for bleaching is necessary, as some materials give a bluish white and others a creamy white. Only scrupulously clean drums, paddles, horses, etc., must be used, otherwise the goods may be stained and rendered quite useless for sports goods, etc.

XV

THE MANUFACTURE OF CHAMOIS LEATHER

Splitting

There is considerable difference of opinion about the respective merits of the band knife splitting machine and the older type of sheepskin splitter employing the reciprocating blade. Although the former possesses considerable advantages as regards speed, it is rather prone to produce linings or splits of uneven thickness, the operator being unable to exercise the same high degree of control over substance as is possible with the older type of sheepskin splitter. For resplitting linings, that is, removing the layer of fat usually taken off by the frizer over the beam, the Reeder is excellent and where band knife machines are used for splitting, some of the old reciprocating knife machines should be reserved for "machine frizing."

The success of splitting depends on several important factors:

1. *Proper liming.* Unless the goods are plump and firm it will not be possible to obtain good linings even if the grain is up to standard. The bellies will be thin and poor and the flanks tapering off to ribbons.

2. *Adequate settling of pelts.* It is altogether a mistaken idea to suppose that goods which are to be split on the band knife require less standing or settling than those to be split by means of reciprocating knife machines. The procedure

recommended by the author is as follows: After machine fleshing, the goods should be piled up and allowed to remain for at least 24 hours. They can then be sorted into various grades according to quality, size and substance. These heaps are taken up by the splitter and his young assistant and slicked or smoothed out with a small tool so as to remove all creases. This is very important as the presence of wrinkles and creases may cause disfiguring cuts to be made in the goods. Carefully slicked pelts should be allowed to remain in small heaps, not more than 7–10 dozen, for 12 hours before splitting.

3. *Accurate sorting.* The importance of this highly skilled operation should be immediately obvious.

4. *Accurate splitting.* To insure real accuracy the first splits of each grade should be carefully examined by the overseer, on whose instructions the gauge must be adjusted.

Reliming for Frizing

After splitting the linings can be graded for resplitting, so as to reduce the necessity for expensive hand frizing over the beam. As a measure of economy this procedure is recommended by a large number of tanners, but it should be pointed out that resplitting cannot entirely replace frizing which not only removes the unnecessary layer of fat, but levels the substance of the entire split.

Before frizing can be carried out properly it is necessary to relime the goods. English tanners generally prefer pit liming, but excellent results can be obtained by means of paddles. Twenty-five pounds of hydrated lime per 100 gallons of water will be found sufficient for the new lime. The procedure should be to run the goods in a used lime liquor, working the paddle wheel for four hours a day for a period of four days. At the end of that time the linings must be

transferred to a sharp, fresh liquor and run for the same length of time. By this time the goods will generally be found nice and plump and in a proper condition to take clean strokes with a frizing knife.

Washing After Frizing

Paddles can be used, but a tumbler is preferable and the author is of the opinion that a polygon shaped one gives the best results. The wedge shaped sides of such a vessel holds the goods in turning, allowing the upper surface only to slide in motion, the skins all being continually opened out and intermixed and "balling" up is impossible. Tanners with experience of this type of tumbler generally agree that goods are much more evenly and quickly washed in it and there is a saving of 30 to 50 per cent in time. Washing should be completed in six hours, running the tumbler with a lattice door and allowing the maximum volume of water to pass through the hollow axle.

Centrifuging

After washing, the surplus water must be removed, either by pressing in a hydraulic press, working at 2½ tons per sq. in. or running in a centrifuge for five minutes. If desired, pressing in the hydraulic press can follow reduced centrifugal action.

Stocking (Dry)

Various types of stocks or pushers are used, such as faller stocks, improved crank stocks, self-contained pendulum stocks, etc. The capacity may vary from 30–140 doz. and the H.P. 2–6 according to size. After removing excess of

moisture and processing the skins so that they are in a nice sammied condition, each split must be well shaken out and the stocks loaded up and the pummelling action started. At the end of three hours the stocks require emptying and the splits hanging up in a cool stove, 65° F., for six hours. Further stocking for six hours should then be carried out so as to work the goods into a fit condition to absorb the oil.

Stocking (Oil)

Good quality Newfoundland cod liver oil is necessary for oil tanning. No figures can be given regarding the amount of oil necessary to tan a dozen splits; everything depends on the size, shape and condition of the goods and the mill foreman has to use his own discretion. Milling or stocking is a very tricky process and a great deal of care has to be exercised in the control of the process. After six hours' stocking in oil the machine should be stopped and the box emptied. Each split or lining must be well shaken out and laid out on the floor to cool for 20 minutes or so. They must then be thrown back into the box and the machine set in motion. A fresh quantity of oil is then added and stocking continued for a further period. Gradually the goods take on the color of the oil and when they have absorbed what may seem the maximum amount of oil, that is, after about four days' stocking, they should be hung up in a hot stove, 125° F., and sealed up for eight hours. Oxidation of the oil proceeds very quickly in the hot, stifling atmosphere of the stove. Before the men enter next morning the suction fan should be started up so as to draw off the choking fumes of acrolein. Further stocking with oil is necessary, taking particular care to avoid overheating the goods. At the end of two hours the oil leathers, for they have reached a leathery stage, should be shaken out and laid out

on the floor to cool. A period of eight hours' stocking should be sufficient and the goods then require another "heat" for 10 hours. Further stocking for four hours without oil is necessary to finish off the process.

The procedure explained above can, of course, be adapted to meet any special requirements. Generally speaking, a week is sufficient to complete stocking.

Pressing

The oil leathers should be dipped in hot water, 165° F., and then packed in a hydraulic press. A pressure of 2–3 tons per square inch is usually sufficient to remove the bulk of the oil, a heavy, dark colored liquid known as degras. Some tanners unload the press after the first pressing, soak the leathers in hot water, 155° F., for one minute and then repress them to get a second and lighter flow.

Washing

This is best carried out in a machine dolly or chamois washer. The action is to thrust the goods by the prodding forks into the soda liquor. The tub revolves slowly, thus bringing all the leathers under the forks. A good dolly will wash 175 skins a day.

Suitable concentration of alkali is 2½ per cent soda ash on the weight of pressed leathers, temperature 130° F. Removal of excess of oil takes 1½–2 hours and it is advisable to work with a used liquor which contains 5–8 per cent saponified oil in solution. This acts as a very satisfactory fatliquor. A fresh alkaline liquor can be rendered ready for use by throwing in some waste pieces of oil leather. If a pure soda solution is used, the chamois dries out on the harsh side and unsuitable for gloving.

Wringing or Centrifuging

Instead of using the primitive wringer, it is advisable to make use of the labor saving centrifuge, running the goods for five minutes. Gloving chamois should be dipped in water 200° F. before centrifuging. This shrinks the leather and gives it the desired characteristics required by the glove manufacturer.

Drying

Goods should be dried under conditions as near natural as possible (max. 70° F.).

Finishing

This is usually quite simple. After staking the goods require fluffing, buffing, and brushing. Sorting and measurement follow in due course.

TIME TABLE OF PROCESSES

Process	Type of Machine	Time	Details of Process
Splitting	Band knife splitter (Width of split 57 in.–106 in.) (Power ⅝ H.P.) (Pulleys 18 in.) (Speed 160 revs.) Sheepskin splitter (Width of split 4 ft. 6 in.)		
Reliming	Paddle	4 hrs. a day for 4 days	25 lbs. hydrated lime per 100 gals. water
Washing	Polygon tumbler Diameter 7 ft. 6 in. to hold about 25 doz. splits Power, 2 H.P. Revs., approx. 6 per min.	6 hrs.	Cold running water
Centrifuging	42-in. machine	5 minutes	
Stocking (Dry)	Faller stocks Capacity, 80 doz. splits H.P., 4 Pulleys, 30 in. x 5 in. Speed, 75 revs.	1st Period 6 hours 2nd Period 6 hours	After 1st period Goods hung up to sam or air off for 6 hrs.
Stocking or Milling (Oil)	Faller stocks	1st day (1st period 6 hrs.) (2nd period 4 hrs.) (3rd period 4 hrs.) 2nd day (4th period 4 hrs.) (5th period 4 hrs.) 3rd day (6th period 4 hrs.) (7th period 7 hrs.) 4th day (7th period 7 hrs.) (8th period 4 hrs.)	Goods shaken out and laid out on floor to cool after each period of stocking.

TIME TABLE OF PROCESSES (Continued)

Process	Type of Machine	Time	Details of Process
Heating Off		8 hrs. in stove	125–135 deg. F.
Stocking		1st day (1st period 2 hrs.) (2nd period 4 hrs.) 2nd day (3rd period 4 hrs.)	Goods shaken out and laid out on floor to cool after each period of stocking. At the end of this 10 hrs.' stocking goods require stoving for 10 hrs., 130 deg. F.
"		1st period 4 hrs.	Goods shaken out and laid out on floor to cool.
Pressing	Hydraulic press Total pressure 460 tons Working pressure 3 tons Platens provided with grooves for taking the oil	Time varies approx. ½ hr.	Oil leathers dipped in hot water 165 deg. F. before pressing. 2nd pressing can be carried out if desired.
Washing	Machine dolly Pulleys, 15 in. x 4 in. Speed, 50 revs. Washes 175 doz. leathers a day	1½–2 hrs.	2½ per cent soda ash on weight of pressed leathers.
Centrifuging	42-in centrifuge	5 minutes	
Drying			Goods dried out in cool stove not more than 70 deg. F.
Finishing			Staking, fluffing, buffing and brushing. Sorting and measuring follow these.

XVI

WHITE WASHABLE LEATHER

Fleshes or Linings

At one time it was thought that aldehyde leather was liable to deteriorate on storage and, in consequence, could not be guaranteed for any length of time. While there is little doubt that this belief was largely due to unreasonable prejudice on behalf of tanners and glove makers who maintained a definitely conservative outlook towards all new fangled methods, there is no lack of evidence that trouble was encountered in the early days on account of the "tendering" of the leather and the difficulty of close stitching in glove making without cutting the leather. The writer considers that aldehyde tannage, if properly carried out, can produce excellent leather of reasonable keeping qualities which are comparable with chrome, but it must be admitted that the margin of safety or latitude allowed the tanner is not as great as with vegetable or alum tannages, which are generally considered to be fairly simple and straightforward.

Fleshes or linings suitable for aldehyde tannages should be of good quality and even substance. Preference is usually given to lambs which have the correct texture for gloving. Careful selection prevents waste and facilitates maximum production of quality grades which give the tanner the best return on capital outlay. Re-splitting to remove excess fat should be carried out if necessary, as it reduces expensive hand frizing later on.

FLOW SHEET OF PROCESS FOR ALDEHYDE LEATHER

Process	Method of Working	Time Taken	Details of Formula Employed
Liming	Paddle	4 hrs. day working for 4 days	3% hydrated lime
Frizing	Hand work		
Re-liming	Pit	48 hours	Mellow lime (no sulphide)
Washing	Polygon drum	4 hours	Running cold water
Deliming	Paddle	¾ to 1 hour, but varies considerably	¾ lb. acetic and ½ lb. formic acid per 100 gallons
Bran Drench	Paddle	8 hours. Start up by working for ½ hour. Rest of time the paddle is stationary	½% bran on limed weight. Water at 85° F.
Pickling	Drum	½ hour	250% water 10% salt 0.5% sulphuric acid (cold water)
De-pickling	Drum	½ hour	10 lbs. ammonium sulphate 25 lbs. sodium chloride 7½ lbs. sodium bicarbonate (per 100 gallons at 97° F.)
Washing	Drum (lattice door)	1 hour	
Tanning	Drum	3 hours	1¼% solution of commercial formaldehyde water at 97° F.
Neutralization	Drum	2 hours	¾% bicarbonate of soda and 200% cold water based on pickled weight or ½% on limed weight.
Washing	Drum (lattice door)	1½ hours	90° F.
Hydro-extracting	Hydro-extractor	4 minutes	
Fat-liquoring	Drum	3 hours	2½% china clay 1½% soap chips 130% water (goods run ½ hour) Add 1½% flour 1½% sulphonated neatsfoot oil (run for 1 hour) Add 1½% egg yolk (run for 1½ hours)
Finishing	Stake and buff		

Liming

Paddle work is recommended, using three per cent hydrated lime on the weight of the goods after splitting. Let the paddle run for four hours a day, two hours in the morning and two in the afternoon, for four days, taking care to poke the skins under the surface of the liquor when the paddle wheel is not revolving. It is advisable to start off with a fresh solution of lime, instead of one which has previously been in use and merely strengthened up before re-use.

Frizing

This operation is just as necessary for aldehyde leather as for chamois and should be very thoroughly carried out. There is no really satisfactory substitute for hand frizing and if it is omitted, then finishing operations become increasingly difficult.

Re-Liming and Washing

Some tanners like to re-lime their frized goods in a mellow lime and this practice is to be recommended. The writer is of the opinion that the best results are achieved by soaking the fleshes in a pit containing mellow, but not stale lime liquor. A period of 48 hours is generally sufficient. Washing in a polygon drum for four hours in running cold water is the next step and this removes most of the surplus lime.

Deliming

Organic acids are recommended for neutralizing the lime and good results can be achieved by use of a mixture of

acetic and formic acids, preferably ¾ lb. acetic and ½ lb. formic acid per 100 gallons of water in a paddle. Lactic acid also gives satisfactory results, the optimum quantity being two lbs. per 100 gallons of cold water. Paddle de-liming is usually preferred.

Neutralization should not be complete, but must be carried beyond the stage recommended for goods which are to be puered or bated.

Bran drenching is not absolutely essential, but the writer is of the opinion that a light drenching, using ½ per cent bran on the split weight, is beneficial. It is best carried out in an open paddle, temperature of water being 85° F., and continuing the processing for ½ hour and then allowing the goods to remain in the solution overnight. Scrud by hand or machine after drenching.

Pickling

Although on the face of it pickling may seem an unnecessary process, as goods have later to be de-pickled, to many tanners it appears to have a beneficial action on the goods and also enables sorting to be carried out, as defects show up very well in the pickle. Recipe recommended is:

250 per cent water
10 per cent salt
0.5 per cent sulphuric acid

Goods should be drummed in this for 30 minutes.

Depickling

There are various methods of neutralizing the free acid present in the goods, but the writer recommends Payne's method. This entails drumming the goods in the following solution for half an hour:

Ammonium sulphate	10	lbs.
Sodium chloride	25	lbs.
Sodium bicarbonate	7½	lbs.
Water at 97° F.	100	gals.

When neutral, as tested by phenolphthalein, the goods should be well washed in running water for one hour, then allowed to drain ready for aldehyde tannage.

Tanning

A good method is the following:

Drum the goods in a 1¼ per cent solution of formaldehyde and 140 per cent water at 90° F. for 3 hours for lambs, 3½ to 4 hours for sheepskins. Some discretion must be used regarding the length of time, this to be determined by the size of the skins, weight alone not always being a safe criterion. It is advisable to start tanning in a ½ per cent solution and to add a further ½ per cent after 30 minutes' drumming until the total amount of formaldehyde is present. The last addition should, of course, be ¼ per cent.

Neutralization

Bicarbonate is recommended as a safe alkali for this purpose, using ¾ per cent on the pickled weight or ½ per cent limed weight. Water should amount to 200 per cent. Drum goods in the weak alkaline solution for 2 hours, then test the cut surface to determine extent of neutralization. While still on the acid side of true neutrality, run off the alkali and commence washing in running water for at least 1½ hours, using water at 90° F. Allow goods to drain for two hours, then hydro-extract lightly and prepare for fat-liquoring.

Fat Liquoring

This is best carried out in stages, starting first with curd soap or textile flakes. Drum the goods in the following solution:

2½ per cent china clay
1½ per cent soap chips or flakes
130 per cent water at 100° F.

It is advisable to dissolve the soap in a small quantity of boiling water and to stir into this the china clay, so as to effect an even dispersion of the particles. This concentrated mixture is run into the water in the drum immediately before the goods are thrown in. After ½ hour, add 1½ per cent flour and 1½ per cent sulphonated neatsfoot oil and continue for another hour. At the end of this period, add 1½ per cent egg yolk and continue for a further hour and a half, making a total of three hours.

Fat-liquoring is a most important process and should take between three and four hours. Allow goods to drain for three hours and then hang up to dry in a cool shed.

Finishing

When almost dry, but containing just enough moisture to work easily, stake and when aired off in a warm stove buff to obtain the fine nap required for high grade gloving leather. Some tanners dispense with machine staking and buffing and, instead, perch and stone by hand. They claim that better results are obtained in this way. If the earlier processes have been carried out properly, there should be very little finishing needed.

XVII

THE MANUFACTURE OF GLACE KID

THE manufacture of glace kid is, without doubt, an exceedingly difficult process, as many tanners have found out to their cost. Success or failure is largely determined by the efficacy of early beam house work, particularly liming and puering. These are key operations of first rate importance. There is only a comparatively small amount of latitude allowed and the tanner must largely rely on his own judgment.

CONDITION OF SKINS

These are usually air dried, earth cured, dry salted or wet salted. The first is carried out in three different ways. For instance, there is open sun drying, shade drying and shed drying. The last named gives the best results as conditions of drying can be reasonably controlled. Sun or flint dried skins often give considerable trouble in the soaks and may necessitate expensive and lengthy breaking down operations. Shade dried goods vary a good deal in quality and wetting back properties, but, generally speaking, they are superior to the sun dried skins. The practice of drying skins in sheds, even if they are only makeshift constructions, is to be recommended on all counts, especially when supplemented by an arsenical dip. In practice it has been found

that good shed dried goatskins can be soaked and processed almost as easily as dry salted goods. The native earth cure is responsible for a good deal of trouble and the cure, while an improvement on sun drying, is too variable to be really useful. Goods are not always properly cured and obstinate stains are quite frequently formed, due to the presence of iron salts in the earthy mixture.

The four most common blemishes found in goatskins are:

1. Flay marks.
2. Hard patches due to bad drying or damage due to bacterial, fungoid and insect attack during drying or storing under humid conditions.
3. Skin diseases and insect damage.
4. Stains and miscellaneous defects.

It is not the intention of the writer to describe these in detail, but it is worthwhile pointing out that some progress has been made in the control of flaying and drying in the main goatskin exporting countries. In Northern Nigeria, for instance, a scheme is in operation which makes it compulsory for butchers to flay in such a manner as not to damage the goods by knife cuts. The sharp pointed knife previously in common use is now replaced by one with a curved blade. In the case of goats and sheep a knife is used only to make a few initial cuts and the flaying is completed by drawing and punching with the hand. According to a bulletin on "The Preparation of Empire Hides and Skins" issued by The Imperial Institute, London, in Nigeria and other skin producing parts of the British Empire travelling inspectors are engaged in touring the districts and in giving instructions to the butchers. This practice is calculated to save an enormous wastage due to carelessness or ignorance on the part of native butchers, often working under the worst possible conditions.

The Bulletin mentioned above states that investigations

into the skin diseases of goats show that the lesions of the various diseases, and more particularly of demodectic mange and streptothricosis, are responsible for blemishes in tanned skins to a varying degree. Apart, however, from the effects of skin diseases, blemishes are also due to thorns and scratches, although goatskins are not so subject to these as sheepskins. Insect damage is not nearly so common as it was ten years ago, owing to the greater care now taken in the preservation of skins, especially the increased use of insecticides, such as naphthalene and various arsenical dips.

Of considerable importance to the tanner is the shape of skins. Queer shapes do not lend themselves to economical cutting up in the shoe factory and, in consequency, do not command good prices. Preference is always given to small, square shaped skins, which not only prove very economical to the shoe manufacturer, but also possess the finest and smoothest grain.

Another consideration affecting the tanner is the amount of grease contained in the skin. The ideal goatskin is one containing the absolute minimum of grease. European goatskins usually contain a much higher percentage of grease than Indian or African skins, although sometimes skins of eastern origin show greasy patches due to the soaking in of natural grease from the carcass, remains of which are left clinging to the skins. Grease interferes with the penetration of the tan liquor to a certain extent, but more particularly leads to trouble during finishing. Skins which are known to be very greasy should be well scudded three or four times, instead of once or twice. Scudding after bating can remove a considerable portion of unevenly distributed grease or excessive grease, as the enzymes present in the bate have an emulsifying action on the fats.

Warehouse Conditions

Bales of goods from the docks should be stacked up in a dry, cool building and it is recommended that they should be kept from actual contact with the floor by means of a low wooden platform built about three or four inches high. This is advisable because it not infrequently happens that the floor is damp or very dirty and, in consequence, there is a risk of skins being damaged. The number affected may appear insignificant, but over a period of years even 0.1 per cent may work out to quite an appreciable figure on the debit side of production. Careful watch should be kept for rodents and insects liable to attack the skins.

Origin of Skins

Goatskins are exported from practically all quarters of the globe, including Northern and Southern Europe, Northern and Southern Africa, Asia, South America, and Central America. The Indian skins, such as Patna, Madras, North Western, and Amritsar, are probably the best known and most highly prized. Consignments from Africa are Algerian, Mogador, Constantine, Berbera, Mogadiscio, Natal, Nigerian, Cape Town, Abyssinian, etc. In normal times a considerable number of skins were exported from China, the best known grades being Tientsin, Hankow, and Chow Chin. A good deal could be written about the characteristics of the different grades, but the author does not propose to devote any more space to them, as his main purpose is to describe the actual processes of glace kid manufacture.

Soaking

A great deal depends on the thoroughness of this process, as it is not possible to complete liming successfully unless

the skins are as soft as when they left the animal's back. This is the ideal to be aimed at by the tanner. The use of old blood soaks, as they used at one time to be called, is far too risky, especially in warm weather, and the writer recommends either chemical or enzymic assistants as being safer. The method commonly adopted in Great Britain is as follows:

The soak pit is cleaned and then filled up to the required level with fresh water. Goods are thrown in one at a time and poked under the water. At the end of 24 hours they should be drawn and allowed to drain for two hours before being thrown back in the water. During the next 24 hours they are drawn three times and then transferred to a pit containing one lb. sodium sulphide per 100 gals. of water 58° F. Draw goods after eight hours and then again after

A BATTERY OF SHAVING MACHINES IN AN ENGLISH TANNERY SPECIALIZING IN GLACE KID MANUFACTURE . . .

16 hours. Allow skins to remain in the solution for two days, draw or haul and dry drum for one hour and follow this up by tumbling in running water for four hours.

At the end of this period the goods will usually be found nice and soft, but in the case of obstinate flint dried skins it may be necessary to resoak in sulphide for a day or so and then to dry drum and wet drum until in the proper condition. Occasionally breaking over the beam with a blunt unhairing knife is the only thing that will soften flint dried skins, but this hand operation is both expensive and lengthy and stocking should first be tried as an alternative method. Fallen or dead skins which are full of blood are often difficult to soften and may require soaking in a stronger sulphide solution. Dry drumming can usually be relied upon to soften most skins, if followed by adequate drumming in plenty of running water. For the convenience of practical men a simple schedule for the various cures is given:

Sun or Shade Dried

Time	Plant Used	Solution	Temp. Max.
1st day	Pit	Clean water	65° F.
2nd day	Pit	Drawn three times. Same water	65° F.
3rd day	Pit	¾–1 lb. sodium sulphide per 100 gals. water	65° F.
4th day	Drum	Dry drum for 1 hr.	65° F.
4th day	Drum	Drum in running water for 2 hours	65° F.
4th day	Pit	Clean water	65° F.
5th day	Pit	Another change of water	65° F.
5th day	Pit	Same water two draws	65° F.

Note: This program may be abridged or continued if required.

Dry Salted

Time	Plant Used	Solution	Temp. Max.
1st day	Pit	Clean water	65° F.
2nd day	Pit	Drawn three times. Same water	65° F.
3rd day	Pit	½–¾ lb. sodium sulphide per 100 gals. Water. Drawn every eight hours	65° F.
4th day	Pit	Drum in running water for three hrs.	65° F.
4th day	Pit	Clean water	65° F.

For wet salted goods usually three to four days' soaking in different changes of water, without sulphide, is sufficient to bring the skins back to their normal condition. Goods must, however, be drawn at least twice a day.

Use of disinfectants in the soak water is sometimes ad-

visable, especially if goods are known to be damaged by bacterial action or in warm, thundery weather, when bacterial action in the soaks is liable to be accelerated. Although phenol can be used, one part per 1,000 of water, it is more economical and safer to use more powerful disinfectants, such as para chlor meta xylenol or para chlor meta cresol in proportions about 500 parts per million. Sodium bisulphite is also a very useful disinfectant, but goods must be freed from all traces of free sulphurous acid before entering the lime.

Unhairing

Soaked goods should be well drained or lightly centrifuged before painting with depilatory. If too wet, the paint will not stick and uneven depilation will result. A suitable depilatory can be made as follows:

Place 1½ cwt. of quicklime into a large wooden tub and just cover with boiling water. When the lime is slaking properly add 30 lbs. of red arsenic and allow to remain for one hour. Pour in sufficient water to make the depilatory the consistency of a nice easy flowing paste. Stir the depilatory with a long pole during the actual preparation.

Apply the paste to the skins on the flesh side, allowing sufficient of the depilatory to cover the full area of the skins. Fold the painted skins down the center of the back and pile up in small heaps at the bottom of a pit. Place planks over and weight down with stones. Fill up the pit with cold water and allow the goods to remain three or four days or until the hair is loose. Unhair by hand or machine.

Liming

A sulphide lime liquor is recommended for the best results, the use of ordinary sodium sulphide being generally

considered prejudicial to the production of fine grain leather. A practical recipe for a sulphide lime is as follows:

1½ barrows of lime (250 lbs.)
12 lbs. red arsenic
5 buckets of boiling water

Slake the lime with the boiling water in a large tub or vat and add the 12 lbs. of arsenic. Stir up the mixture with a pole and continue stirring until the lime sulphide solution is cool. Now put in a clean pit 160 lbs. lime and enough water to slake it. Allow it to remain for eight hours, that is, until next day, then fill up the pit to the required level with cold water. Pour in the prepared arsenic sulphide and lime solution and then plunge up the pit preparatory to throwing in the goods. Generally liming is carried out first in a used or mellow sulphide liquor and then in a fresh solution made up as above. Usually three days with two draws a day in the used liquor is sufficient. This should be followed by three or four days in the fresh lime. When liming has been carried out to completion, the goods require trimming or rounding to remove all offal and then fleshing by machine.

Some tanners start off the liming by processing the goods for one day in an old or stale lime, i.e., one that has been used for two or three packs. They claim that the resultant leather has more of a silken grain than can be obtained by any other method. The author is of the opinion that equally good results can be obtained by wise use of mellow instead of old limes.

Washing

The drum is generally preferred for this and the writer considers that the polygon shaped vessel is to be recommended as washing is more thorough. Drumming in cold running water should be continued for four hours.

Deliming

Boric acid is the most suitable material and should be used in proportions of 15 ounces per 100 lbs. of stock. The paddle is preferable to the drum and the amount of water employed is not of such great importance. Deliming should be continued for 2½ hours and be followed by thorough washing in running cold water in a large paddle where the goods have plenty of room to move about.

Puering or Bating

Some tanners do not make use of a deliming process, but consider that a four hour wash is sufficient to remove the bulk of the lime, the remainder being neutralized in the puer. In this case bating has to be carried out somewhat further than would be necessary for delimed goods.

Nowadays dog dung is seldom used, although it gives better results than artificial bates. The disadvantage of the natural excrement is that it is somewhat difficult to control and standardization of the process is impossible, whereas, of course, with artificial materials it is comparatively easy to regulate bating within reasonable limits. Proportions of enzymic bate vary somewhat with different types of goods and the degree of bating or falling desired. A useful method consists of dissolving 18 ounces of bating material per 100 lbs. of limed stock in a sufficient water at 95° F. Allow to digest for 48 hours, then heat up to 97° F. and throw in goods for a day and a night. Run the paddle for short spells during the day. Next morning examine the goods and, if not fallen sufficiently, add a further six ounces per 100 lbs. of stock and heat up to 97° F. and continue paddle action until fallen.

Scudding

This should, if possible, be carried out by hand, but some tanners prefer first to scud by machine, then soak in warm water 97° F. and scud by hand over the beam. The importance of thorough scudding cannot be over emphasized, as only by this means is it possible to remove all the short hairs left over from the unhairing process and to work out the maximum amount of excess or unevenly distributed fat. It is false economy to dispense with scudding and machine scudding cannot, in the writer's opinion, completely supplant hand work.

Washing

Paddle washing in plenty of running cold water should be carried out for two hours after bating, to remove all traces of the puer liquor.

Bran Drenching

While some tanners dispense with this operation and pickle the puered and washed goods, the writer is of the opinion that drenching should not be omitted, but that pickling is not absolutely essential even if it is desirable, which is by no means certain. A suitable drench may be made by using two lbs. of bran per 100 lbs. of stock. First of all clean out the drench paddle by sterilizing with boiling water or steam and then fill up to the required level with water 98° F. Allow the bran to digest for four hours and then put in the goods. Move the paddle wheels round by hand for a few turns and then leave for eight hours. In warm and thundery weather four hours will generally be found sufficient. Wash in cold running water for one hour, when the goods will be

ready for the two bath chrome tanning. It is sometimes a good plan to scud very greasy skins from the drench.

TANNING

After draining for half an hour or so, the skins should be thrown into a drum and for each 100 lbs. of stock the following two solutions run in through the hollow axle of the drum.

No. 1—2½ lb. bichromate, 1½ lb. hydrochloric acid, 4½ lb. common salt dissolved in 7 gals. water.

After ½–¾ hour drumming a stronger yellow should be added made up by dissolving:

No. 2—3½ lb. bichromate, 2½ lb. hydrochloric acid dissolved in 7½ gals. water.

After four to five hours, the yellow will have penetrated right through the center of the skins. They should then be horsed up, grain to grain, covered up and left for eight hours. Next morning the skins will require striking out on the vertical table machine ready for reducing or "blueing." This is preferably earried out in stages. First of all, the skins should be passed through a weak reducing bath to set or fix the chrome. This can be made up in a large vat or stationary paddle by dissolving four lbs. hypo and 2¼ lbs. hydrochloric acid in 10 gals. water per 100 lbs. of stock. Transfer the goods from this bath to a drum and straightaway commence reducing by running on 15 lbs. hypo and seven lbs. acid dissolved in 20 gals. water per 100 lbs. of stock. Reduce for 3½–4 hours and then run on a further quantity of reducing solution made by dissolving 2½ lbs. hypo and 1¼ lbs. acid in 5 gals. of water and continue for another 3½ hours. (All these quantities are based on a unit of 100 lbs. limed stock.) Horse up goods, grain to grain, for four to eight hours on horses or in zinc trays. When well drained, weigh.

Washing and Neutralizing

First wash for two hours in a drum, using plenty of running water, and then neutralize with two lbs. borax per 100 lbs. of chromed goods. Dissolve the borax in 5 gals. of boiling water, allow to cool and then add to the drum in two portions. Usually one hour is required for neutralization and this should be followed by washing in running water for 1½ hours. Horse up, grain to grain, and allow to drain ready for dyeing.

Some tanners strike out goods in the blue as well as in the yellow, and this is a good practice, provided it is carried out after the leathers have been allowed to settle. Skins must be shaved to level the substance, particularly to thin down the neck. Weigh goods ready for dyeing.

Dyeing

Prior to the introduction of direct chrome dyes, the dyeing of colors, particularly light shades, was always a difficult and uncertain process. Nowadays, however, there is no reason why dyeing chrome goat for glace should prove any more difficult than any other class of chrome leather. It is not proposed to give recipes, as these are meaningless without patterns, and, in any case, dyes used in Great Britain are not readily obtainable in the United States. The method of dyeing recommended by the writer will, however, be treated at some length.

For blacks, good results can be obtained from logwood, copperas, and nigrosine, but the author recommends the use of a direct black instead of the acid dye. Useful proportions are 2½ per cent logwood crystals on the shaved weight dissolved in boiling water, cooled to 140° F., and then slowly

poured into the dyeing drum through the hollow axle. The temperature of the water in the drum should be 130° F. At the end of 20 minutes, 2¼ ozs. per cent of copperas dissolved in two gals. of hot water, 140° F., should be added and the drum run for 15 minutes. The direct chrome black, approximately ¾ lb. per cent to 1 per cent, should then be dissolved in two gals. of boiling water, strained, cooled to 140° F., and added in two portions, ½ hour being allowed before adding the second portion. At the end of one hour goods should be dyed a nice black.

If nigrosine is preferred to chrome black, then it is advisable to add a little ammonia, about 0.1 per cent by weight of concentrated ammonia, after running in the nigrosine for ¾ hour. This increases penetration.

For colors use 2 per cent fustic for tans, 1½ per cent fustic and 1½ per cent logwood for dark brown, 2 per cent sumach extract for buffs, peach and other delicate colors. Proportions of dye vary from 12–18 ozs. per cent. Shades of grey and other popular colors can often be obtained by use of direct chrome dyes and a soap bath.

FAT-LIQUORING

This is best carried out in the same drum and liquor as used for dyeing. It is, however, advisable to heat up the liquor with a steam pipe if the temperature has fallen below 120° F. For blacks, a combination of olive oil soap, neatsfoot oil, sperm oil, and borax gives good results. Recommended proportions are:

1 per cent olive oil soap.
2 per cent neatsfoot oil.
½ per cent sperm oil.
2¼ ozs. per cent borax.

Colors need slightly different treatment, preferably a recipe built up on the following lines:

1½ per cent olive oil soap.
1 per cent castor.
½ per cent sperm.
2 ozs. per cent borax.

Sulphonated oils are not recommended, as they tend to give the goods a flannel-like feel, which is very undesirable.

Fat-liquoring must be continued for at least ¾ hour and preferably more, when all the fat should be absorbed. Goods then need washing up in tepid water, approx. 85° F., allowing to drain on horses for two hours, followed by striking out and setting. After setting the leathers require smearing over with glycerine one part in 10 of water, either by hand or by means of a glycerine machine. Drying is usually done on poles in a hot stove or in a drying machine.

Finishing

When bone dry, the goods benefits considerably from aging in a cool shed for several days. They can then be piled in damp, clean sawdust and left until in the proper condition for staking. Afterwards they must be aired off, fluffed or buffed, then restaked.

Use a four to five per cent solution of lactic acid for normal skins or one made up of four parts of water and three parts lactic for rather oily kid. Brush on the grain and then allow to air off. Repeat if necessary. Lactic acid is preferable to formic, although some tanners use a 2–2½ per cent solution of this acid.

Seasoning

There must be hundreds, if not thousands, of different recipes, all of which are claimed by their originators or users to give excellent results. A working formula is the following:

No. 1—Dissolve 1 lb. hematine in 4 gals. of hot water, 150° F. Add to this 7 ozs. nigrosine dissolved in 1 gal. boiling water. Boil the mixture by means of a steam pipe and then add ½ pint glycerine.

No. 2—Separately dissolve 20 ozs. of egg albumen in 3 gals. of lukewarm water and then add to this solution 5 ozs. prepared casein and 1 pt. of blood. Make up to 5 gals. and add a small portion of a suitable disinfectant, say, ½ oz. of parachlormetacresol.

Mix Nos. 1 and 2 when cold and strain before use.

Season goods, air off or dry, glaze twice, reseason and lightly reglaze, iron or warm press, and smear over with a little warm spindle oil. Hang up to dry, measure and dispatch to warehouse.

The above operations must, of course, be adapted to meet the peculiar conditions appertaining at the time.

XVIII

DRESSING REPTILE SKINS

REPTILE skins of interest to the tanner include lizard, snake and alligator. The most important sources of supply are Africa, America, Asia, and Australia, and in the Report of the Advisory Committee on Hides and Skins, Imperial Institute, London, 1933, an exhaustive list is given of the principal varieties of skins and the origins of present supplies. Generally speaking, the value of lizards depends on their markings. Distinctive markings are worth a good deal more than skins with little or no markings. The grain, whether prominent or flat, fine or large, is considered in conjunction with markings. In the case of snakes, it is the scales which influence quality and, therefore, price. Smaller scaled snakes are to be preferred. According to the Report mentioned above, only the belly part of alligator skins is usable for leather. The hard, bony scutes on the back are of no commercial value.

Lizard, snake, and alligator skins arrive at the tanners in various conditions—dried, wet salted, dry salted, and cured by means of various arsenical preparations. In some cases the sun dried skins are smothered with naphthalene to prevent insect damage, and these are often particularly difficult to soak down and soften.

SOAKING

This operation is of great importance, and unless carried through to its proper conclusion, future operations cannot

be successfully completed. Some tanners use acid and some alkaline soaks, but the best and safest are the latter, taking care, of course, that undue swelling is avoided. If acid soaks are used, there is a grave risk of interfering with the subsequent bating process. The procedure recommended by the author is to soak the goods in a pit containing 1½ lbs. fused sodium sulphide per 100 gallons cold water. At the end of eight hours they should be drawn out of the pit, the liquor well plunged up or otherwise agitated, and the goods thrown back again one by one. After 24 hours' soaking the skins should be ready for wet tumbling, using the polygon tumbler and processing for at least 20 minutes. A further soaking in strengthened sulphide, adding ¼ lb. sulphide (dissolved in 20 times its own weight of water) per 100 gallons water is then necessary.

In 24 hours' time the goods should be really soft, but if they are still on the hard side, and they may be if badly cured, they must be worked in the tumbler for another short spell and in extreme cases it may even prove necessary to break them over the beam with a blunt unhairing knife. Sun dried skins, to which are attached a good deal of flesh and fat, especially the latter, which soaks into the skin and forms very obstinate patches, benefit considerably from this manual operation and it can be thoroughly recommended in spite of its high labor cost. Indeed, the writer has yet to hear of another equally efficient method of softening obstinate goods.

Liming

On no account should the skins be limed before thoroughly softening in the soak. It is quite impossible to hurry along this type of goods and attempts to do so usually end disastrously. Liming is best carried out in a paddle, making

use of a mellow or used lime to commence with, preferably one that has been used only once before. Use of a stale or old lime is inadvisable, as bacterial damage is liable to be excessive. Paddling in the used liquor should not be more than two hours a day. After three days the goods can safely be transferred to a fresh, sharp lime made up as follows:

5 per cent hydrated lime
1½ per cent sodium sulphide } on dry weight of goods.

Some tanners add 5–10 per cent salt and claim that the addition reduces excessive swelling and improves the handle of limed goods; good results may, however, be obtained without the addition of any salt. Paddle for three hours a day for seven days and then if the scales are loose and the flesh easy to remove, the skins can be taken out and worked over the beam. It is quite impossible to carry out these operations by machine and careful hand work alone can achieve the best results. After fleshing the skins require hand scudding and reliming in a fresh saturated lime made up by mixing six per cent hydrated lime in a paddle of water, the percentage of lime being based on dry weight of goods. It is advisable to re-lime for three days, working the paddle for a maximum of four hours a day. It is necessary to rescud on completion of the liming process.

Washing

This is best carried out in a large polygon drum through which a constant stream of cold running water is allowed to pass. Great care must be taken to avoid risk of knotting or "balling" up of the skins, especially snake, which is liable to be rather troublesome.

Deliming

This can also be carried out in a drum, using 1½ per cent borax on the limed weight, and drumming for 1½ hours.

Bating

Any good enzymic bate can be used, employing approximately four per cent on the dry weight of goods. Either a slow revolving tumbler, not more than two revs. per minute, or paddle should be used, preferably the latter, as it allows closer supervision of the operation. After bating, washing in cold water is necessary for 10 minutes.

Pickling

For making up a fresh pickle for reptiles the following recipe is recommended:

3 per cent sulphuric acid
20 per cent salt
150 per cent water (cold)
} on dry weight.

Drum the goods in this liquor for 30 minutes, then allow to drain and transfer to strong brine solution, 20° Twaddle, for 20 minutes. If goods are to be alum tanned, pickling should be omitted and a bran drench substituted. After draining, the goods should be weighed.

Vegetable Tanning

Excellent results can be obtained by use of sumach extract followed by bleaching with a suitable synthetic tanning material. Tanning is very simple and can be best carried out in a drum using

5 per cent sumach extract	}	on pickled weight.
1 per cent sodium acetate		
150 per cent water		

Run goods for six hours and then stand for eight. Add 10 per cent sumach extract and run for eight hours and stand for ten. Next add another 10 per cent extract and drum until tanned. After draining for 24 hours drum in

10 per cent synthetic tannin
150 per cent water

Choice of synthetic tanning material is very important. There are a number of excellent bleaches available which clear the yellowish stain of the leather and insures a very satisfactory white. (The spent sumach liquor can be strengthened and used for the next pack.)

Alum and Gambier Tanning

Drum in a liquor made up of

5 per cent gambier	}	percentage on pickled weight.
2½ per cent salt		
2½ per cent alum		
200 per cent water		

After six hours add a further 2½ per cent gambier and one per cent alum. Drum for four hours and then allow goods to stand for eight hours. Continue drumming when liquor is strengthened with a further 2½ per cent gambier and one per cent alum. At the end of three days the skins should be tanned, but if penetration is not complete, a further 2½ per cent gambier may be used without the addition of any alum.

This tannage produces a very light colored leather, soft and with a good handle. It is, however, unsuitable for reptile skins which have to be finished pure white.

ALUM TANNING

One of the most useful methods of tanning is carried out with alum. If goods are pickled they must first be depickled with borax and tested with a suitable indicator to determine degree of neutralization, which should be slightly on the acid side. Alum tanning is preferably carried out in a drum, but some tanners consider that the best results are obtained by use of a large barrel or vat, occasionally stirring the skins around with a wooden pole. True, this method takes considerably longer than drum tannage, but there is, of course, no danger of the goods getting entangled and knotted. In the author's opinion, drumming need not necessarily cause trouble if the goods are examined from time to time and, in any case, the drum should be fitted with shelves and not pegs, which often cause knotting. Quantities of alum, salt and other chemicals must be based on the limed weight of goods. A suitable recipe is as follows:

5 per cent aluminum sulphate
4 per cent salt
1 per cent sulphonated neatsfoot oil
10 per cent flour
3 per cent china clay.

These various ingredients should be made up into a thin paste with cold water and goods processed in it for four days; drumming three hours a day and taking care to see that when the drum is stationary the skins are poked under the liquor. At the end of that time the goods must be taken out and horsed up to age for 12 hours. They can then be returned to the drum for feeding. The feeding or fat-liquoring recommended is completed in two stages, the first of which takes place in the spent liquor replenished by the addition of the following:

3 per cent flour
1½ per cent sulphonated neatsfoot oil.

Drum for eight hours, then take out goods and drain for 12 hours. Complete the feeding process by drumming in the following mixture in a clean drum:

10 per cent china clay
5 per cent flour
4 per cent egg yolk
½ per cent neatsfoot oil
(Sufficient water to make a thin paste).

Drum for six hours, drain for 12 hours and then hang up and dry. While still damp, goods should be thoroughly staked and dried slowly in a warm but not hot stove. Then follows fluffing or buffing on the flesh side. Brush thoroughly on the grain. Finishing is usually very simple and, indeed, some tanners merely roll or warm press before measuring. Throughout the processing every effort must be made to retain the spotless whiteness of the goods.

XIX

PARCHMENT

The pelts intended for parchment should be very carefully selected. Points to watch are scab, obvious barbed wire scratches, creases, cockle, and uneven substance. Loose or "pipey" pelts are also most unsuitable for parchment and goods must be firm and with a tight, sound grain. It is necessary for the sorter to exercise the greatest care in the selection of goods for this work and his axiom should be "as near perfection as possible." The best parchment is made from pelts depilated by sweating or use of one of the now well known enzymic depilatory agents. Both these methods are non-staining. The use of sodium sulphide is not recommended, as it is liable to cause obstinate stains which sometimes show up on the finished parchment.

After trimming, cobbing, washing, and scudding, the stock is ready for liming. A start should be made in a mellow lime through which three packs have been drawn. After a week in this, with one draw a day, the goods must be piled up and left for eight hours, taking care to cover the piles over with sacking soaked in lime water.

Now lime in a new sharp liquor containing 1¼ cwt. of lime to the average pit. See that the solution is properly agitated before the pelts are thrown in and then leave for 24 hours. Draw once a day for a week. Drain for two days. Next flesh by machine, allow to settle for at least eight

hours, and then split. Re-split or frize the linings to remove fat.

Before splitting, the pelts must be very carefully slicked out so that all creases and foreign matters are removed. Lime in a sharp clean lime made up of 1½ cwt. of lime per pit for three days, with one draw a day; drain for four hours. Wash linings in running water for one hour, then soak in a large tub containing water at 90° F., for one-half hour; scud by hand. Toggle dry the scudded pelts and allow to dry slowly but evenly. It is important that the parchment should not be dried out in an uneven draft, otherwise contraction may result and cause cracks or creases to appear.

As the parchment dries out, a certain amount of grease will show, and this must be removed. Various methods are available, but the best is to scour the surface with five per cent borax solution, temperature 120° F., using a clean, stiff brush. Rub the skins dry with clean rags and then dry out in a warm stove. The bone dry parchment may next be finished off with a moon knife and finally pumiced to give a smooth and even surface.

The production of parchment and, incidentally, vellum as well, is very simple, but its simplicity is often misleading, as unless every precaution, no matter how insignificant, is taken, then the success of the whole process may be jeopardized.

Chrome Calf (Box and Willow)

On arrival at the tanner's yard, bundles of skins are sorted and the various grades carefully weighed. Full particulars of the sizes, qualities and weights are entered on the order card which accompanies the pack throughout the entire processes. The most common defects in calfskins are flay marks, including holes; insect damage, particularly warble; dung or brine damage; salt stains or salt sprout;

grain damage due to disease or barbed wire, brands, etc., and kippiness. The sorter must be fully experienced and know instinctively by the superficial appearance and weight the kind of skin he is handling and whether it is suitable for the particular class of leather to be manufactured. With wet salted goods it is comparatively easy to arrive at a quick decision regarding value, as gouge marks are readily discernible and many grain defects can be detected by the appearance of the hair side, especially in the case of mange, brands, etc. With dry salted goods, however, quick assessment of value is more difficult and requires a good deal of experience and even then it is not easy, especially if skins from several different sources of origin are being sorted. It is, of course, the wisest course for the tanner to concentrate on as few different sources of origin as possible, so that the characteristics or peculiarities of each kind can be known beforehand by the sorter. This practice makes for standardization of production, which is an ideal aimed at by every tanner.

Mechanical damage, such as fine barbed wire scratches, is very difficult to determine if the scars are old ones and the hair has grown around them again. The skins may appear to be of excellent quality and the disfigurements only become obvious in the pickle or perhaps not until they reach the finishing table.

The European tanner specializing in good quality box and willow usually works with wet salted goods purchased from local hide and skin markets and average about 10 to 14 square feet. After sorting, the old salt is usually brushed off the skins and the goods resalted with clean salt. This practice is recommended because it obviates the risk of salt stains.

Soaking Wet Salted Skins

Goods are first soaked in an old soak through which two packs of goods have passed. After two hours in this liquor

they are then drawn and put into clean water for 24 hours, then drawn and put into another soak of fresh water for a further 24 hours.

Soaking Dry Salted Skins

Goods generally need soaking in an old soak for eight hours. They should then be drawn, allowed to drain for two hours, and then re-soaked in cold water for 24 hours with two draws. They should next be dry tumbled for one hour and soaked in clean water until perfectly soft and clean.

Depilation

Properly soaked goods should be thrown one by one in a pit made up as follows:

220 lbs. quick lime.

22 gallons sodium sulphide solution, 26° Twaddle.

The pit is well cleaned out, the bottom just covered with water, the lime then added and the slaking allowed to continue for 12 hours. The pit is run up with clean water, well plunged up, and the sulphide added. It is advisable to leave the liquor to mix for some hours before it is finally plunged up and the goods thrown in.

Skins are thrown in the sulphide liquor first thing in the morning and left for 2½ hours. Goods are drawn and allowed to drain for one hour. The liquor is then strengthened by the addition of five gallons of sulphide liquor, 26° Twaddle. The pit is well plunged up and goods again introduced and left for a further two hours. They are drawn and sulphide added according to the condition of the goods. Skins are thrown back one by one into the strengthened and well plunged up liquor and left until the next day, when the goods are ready for unhairing.

Unhairing

Nowadays most tanners use an unhairing machine, but in the writer's opinion, the best result can only be produced by hand, using blunt unhairing knives.

Liming

The lime liquor is made up with 220 lbs. quicklime. First the lime is slaked, left for 12 hours, and then the pit made up to the required level with cold water and well agitated or mixed by thorough plunging up. Goods are thrown in and given one draw a day for three days. After that they need only one draw in two days. Leave for a week or until sufficiently limed. Trim and flesh by machine.

Scudding

Hand scudding is recommended for the best results. After fleshing, goods should be soaked in weak fresh lime liquor in large tubs for an hour or so and then scudded by hand to remove all fine hairs, filth, fat, etc. Care must be taken to protect the grain side of the skins and so prevent them from blasting.

One of the most important purposes of scudding is to remove the pigment or color, which, if it is not removed, is liable to cause dark and objectionable patches when the leather is dyed.

Puering or Bating

This is invariably carried out with a good enzymic bate, using eight pounds of bate to 12 dozen goods. The tempera-

ture recommended for this operation is 106–108° F., and it is best carried out in a paddle with the wheel revolving at about 22 revolutions per minute. The optimum length is approximately 1⅓ hours, and throughout this period the paddle should be boxed in so as to conserve heat and maintain the temperature.

Washing

When properly bated, the goods should be washed in running cold water in a paddle for 20 minutes. There is no necessity to use boric acid or any other chemical in the wash water.

Pickling or Rising

A suitable pickling solution consists of a decinormal solution of sulphuric acid and 10° Twaddle salt content. The liquor should be tested for acid content by simple titration before carrying out the process. Generally 1⅓ hours are sufficient to pickle goods.

Falling

It is recommended that all pickled goods should be put into a concentrated solution of strong brine 22–24° Twaddle for ½ hour. Soaking in strong brine reduces swelling and enables goods to be stored for a long time without fear of deterioration. After falling, the skins must be allowed to drain for several hours before spreading out on horses ready for inspection.

Sorting Pickled Goods

It is most important that goods should be properly sorted in this condition as all defects can be seen and a proper as-

sessment made of the suitability of the skins for the type and quality of leather to be manufactured. After careful grading, a pack of 800 or 1,000 lbs. should be made up. This is generally considered to be a very useful load.

Tanning Goods for Box and Willow

For a pack of 800 lbs. pickled weight, which is an average drum load, 50 gallons water 100° F. and 50 lbs. salt are used. Goods must be drummed for 30 minutes. After drumming for the required time, the salt liquor should be run off and skins allowed to drain. After replacing the bungs, a chrome sulphate liquor is run on. This liquor should have a basicity of 80 and contain 135 grammes chrome per litre. Run for two hours, then tray up in large zinc covered trays until next day. Next day wash in cold water until wash water is clear. This generally takes about 1½ hours. Drum goods in weak borax solution, 36 lbs. borax to 50 gallons water (cold). Run for 45 minutes and wash for one hour. Drain off the water and run on a re-tanning liquor. This should consist of the used chrome liquor utilized for the first part of the tanning together with four gallons of strong Batch liquor diluted with 10 gallons of cold water. Run for two hours or until thoroughly tanned. Wash until running water is perfectly clear (1¾ hours); neutralize with 26 lbs. borax. This generally takes about ¾ hour or until cut surface of leather is just faintly acid as tested by litmus. Wash for one hour in water 95° F. Horse up ready for striking out. After this operation, shave down the back or neck.

Dyeing Box and Willow

Most tanners generally prefer to carry out the dyeing process in the drum, as drumming renders possible a better degree of penetration and also economizes in the use of dyes

and other chemicals. On the other hand, however, it has to be admitted that there is a tendency for drum dyeing to cause the grain to be drawn or "grinny," especially if goods are inclined that way. This problem of how to avoid drawn or "grinny" grain is an acute one with some tanners, but the writer considers that, provided care and attention is given to setting and striking out and goods are toggle dried, the trouble can be very largely overcome.

A method which can be thoroughly recommended can be carried out as follows:

For 100 *lbs. shaved weight of leather.*
2 lbs. hematine.
100 lbs. water at 140° F.
Run for 15 minutes, then add
1 lb. direct chrome black.
Dye for a further 20 minutes.
Fix with 2¼ oz. per cent titanium for 15 minutes.
Drain off liquor and top with ½ lb. basic black, 75 lbs. water 140° F., 15 minutes.

The above gives excellent penetration and even color on both flesh and grain. Another method entails use of hematine, nigrosine and an iron salt, but the writer is of the opinion that the use of ferrous sulphate leads to trouble, as it not only tends to exaggerate drawn grain, but also adversely affects the aging properties of the finished leather.

A useful recipe for dark brown willow is:

2 lbs. fustic.
1 lb. hematine.
¼ lb. peachwood.
100 lbs. water at 140° F.
Run for 15 minutes, then add acid dye and run for further 20 minutes.
1 lb. acid brown.
Fix with 2 oz. titanium potassium oxalate for 15 minutes.
Drain off liquor and top with ½ lb. basic brown dye, 75 lbs. water at 140° F., 15 minutes.

Seasoning

Wash first with a dilute solution of lactic acid made by diluting three parts of lactic acid with four parts water. Al-

low to air off and season by hand with a pad, taking care that the solution is worked down below the grain. A suitable season for box can be made up as follows:

No. 1—
½ lb. hematine.
½ lb. nigrosine.
½ oz. ammonia.
4 ozs. methylated spirits.
2½ oz. glycerine.
Dissolve in 2½ gallons water.

The above should be made up by first dissolving the hematine and nigrosine in boiling water, straining the dye, and then, when cool, adding the other ingredients.

Mix the whites of eight eggs in 1½ quarts of bullocks' blood. Stir well and add to No. 1 solution. Dilute the season to make five gallons of liquor.

Another and well tried recipe for box is the following:

No. 1—One quart of logwood solution made by extracting logwood chips with boiling water.
1 quart water.
4 wine glasses glycerine.
2 wine glasses methylated spirits.
1 wine glass ammonia.
No. 2—Place in a bowl the whites of 6 eggs in 2 quarts blood, mix up well and add to No. 1.
No. 3—Now boil 4 oz. nigrosine, ¼ oz. oxalic acid, 2 drachms concentrated chrome solution in 1 pint water. When cold add to No. 1, mix thoroughly, and strain before use.

For willow calf, a simpler season serves the purpose very well.

No. 1—
1 lb. egg albumen.
8 ozs. methylated spirits.
2½ ozs. glycerine.
1½ gallons tepid water at 95° F.

Separately dissolve ½ lb. acid dye in ¼ gallon boiling water, strain, cool and add to No. 1. Now add 1½ quarts of milk to the season, mix well and use.

After seasoning with a sponge, air off, re-season, air off

and glaze, stone or lightly stake, re-season and re-glaze. Grain on machine or by hand, re-glaze and then re-grain and press ready for measuring and the warehouse. There are, of course, a number of alternative methods of carrying out this finishing process, but the above gives good results and a fine grain. For a coarse grain the final glazing after boarding can be omitted.

Fat Liquoring

This should always be carried out in a drum using 3¼ per cent fat for box and 2¾ per cent fat for willow. Optimum temperature 140–145° F. A good fat liquor for both box and willow can be made up as follows:

Add 5 gallons water and 5 pounds of good curd soap to a steam jacketed pan and boil for 1 hour. Add 1½ pounds of borax and continue boiling for ½ hour. Add a further quantity of fat, either degras or neatsfoot oil, 1 gallon, and boil for another hour with constant mixing so as to effect perfect emulsification of the fat. Use the required proportions of the solidified fat.

In place of neatsfoot oil or degras, some tanners prefer to use a mixture of sperm oil and neatsfoot oil in equal proportions. Choice of oil must be determined by the type of leather being manufactured.

After fat liquoring for ¾ hour, goods should be taken out of the drum and left to sammy for two hours; then struck out by machine, passed through a glycerine machine, allowed to remain horsed up grain to grain for three hours, and finally handset ready for straining, preferably by the toggle method.

When dry, hang out in an open shed to season for five hours; sawdust ready for staking. Strain in a hot stove, fluff and season.

XX

DRESSING EAST INDIA GOAT FOR MOROCCO

By far the bulk of the East India tanned goatskins imported into Great Britain are used in the manufacture of morocco for upholstery, bookbinding, bag and wallet work, slippers, and general fancy goods. Choice of skins for these various purposes depends to a large extent on fineness of grain; coarse grained crust leathers are only suitable for bold grained morocco used in the bag, wallet and slipper trade, etc., and to a certain extent for upholstery, although medium grained skins are preferred. Fine grained leathers are in demand for bookbinding.

The best E. I. goatskins for morocco are square shaped skins of a good clean pale color, even substance and nice firm grain free from any tendency to be "pipey." Skins showing obvious signs of being overloaded with grease, clay and other weight giving adulterants should be degreased in a petroleum degreasing plant, but degreasing for all types of goods is not advocated.

It should be realized at the outset that although E. I. goat is extensively employed for bookbinding and upholstery, it is by no means ideal for these applications. The Sub-Committee formed in 1900 by the Royal Society of Arts to inquire into the decay of book bindings came to the conclusion that "red rot" was due to the use of catechol tannins,

such as turwar bark and myrobalans, which are, of course, extensively employed by Indian tanners. It is, however, possible to improve E. I. goatskins to such an extent as to insure a reasonable life for the finished leathers, but it is as well to point out that this cannot be compared with the life of a pure sumach tanned morocco, probably the most durable of all leathers. The Sub-Committee found that stripping, scouring, souring and retanning of E. I. leather were processes definitely prejudicial to the life of the book binding. The writer considers that in the case of stripping or scouring this should be carried out with borax or soap and souring or clearing omitted altogether. Retannage is necessary, but if sumach is used and goods well rinsed afterwards there is not so much risk of overtanning as when using concentrated extracts, such as myrobalans.

Dealing now with the actual processing, the following method is recommended. Goods are carefully sorted, trimmed and weighed. If skins require shaving down the back or neck they should be soaked in warm water, 95° F., and allowed to sam for at least four hours before shaving. Goods to be shaved should first be lightly buffed to clean up the leather. Unfortunately, most vegetable tanned goods show signs of iron stains after shaving and these can only be removed by clearing with sulphuric acid.

Wetting Down and Stripping

This is best done with borax or soap; the latter removes more grease than borax, but somewhat less tannin matter. Goods should be thrown into a drum containing water at 95° F. and run for 15 minutes. The wash water should then be thrown away and a fresh quantity poured in, the same temperature being maintained.

After running the drum for a few minutes the soap or

borax may be added, dissolved in a gallon or so of warm water. The proportions recommended are two per cent borax or 1¾ per cent textile flakes (a good neutral curd soap). Good results may also be obtained by the use of one per cent borax and ¾ per cent soap, the alkali being dissolved in the soap liquor. Stripping, or scouring as it is sometimes called, should be continued for 15–20 minutes.

Washing

This must be very thorough and preferably carried out in a large tumbler provided with a lattice door with all the pegs knocked out. The maximum amount of cold water should be run in and drumming continued for 15 minutes.

Clearing or Souring

Unless absolutely essential, that is, if iron stains have to be removed, the use of sulphuric acid is dangerous. The strength required for effective clearing is ¼–½ per cent sulphuric acid D.O.V. Considerable improvement can be effected by means of formic acid, approximately ¾ per cent on the crust weight.

After clearing in acid the goods must be very thoroughly rinsed before sumaching.

Sumaching

This is preferably carried out in a drum into which is run the minimum quantity of water necessary for the skins to be processed. From 8–12 per cent sumach (dependent on the condition of the goods) should be sufficient to replace the tannin and fillers removed by stripping and rinsing. If the amount of water used has been considerably reduced, then

the drum should be stopped every 10 minutes or so and the door opened and goods allowed to cool off. The time for processing should be about ¾–1 hour and the temperature of the liquor 95° F. The use of ground sumach leaf is preferably to extract, as the latter has not the feeding properties of the natural tannin. Some tanners specializing in morocco for upholstery where a well nourished and rather plump leather is required, add about two per cent of coarse oatmeal to the sumach infusion. The oatmeal helps considerably to build up or fill the leather and improves its handle; on the other hand, it in no way interferes with subsequent processing. After retanning the goods should be washed up in a tank of clean cold water and then stacked on a wooden horse overnight. This settling or samming improves the quality of the leather and should not be omitted.

Dyeing

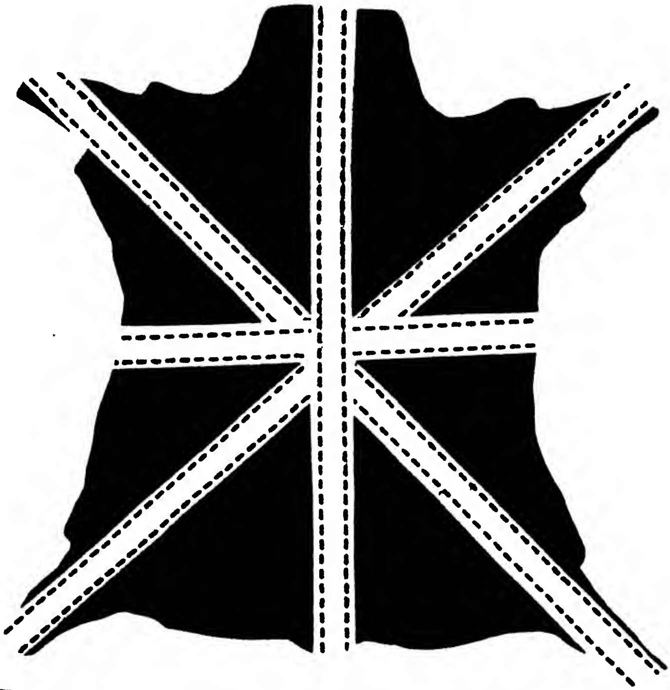
When fastness to light and rubbing is required it is recommended to use a combination of acid and basic colors, preferably bottoming with basic and topping with acid colors, the latter being more resistant to rubbing than the basic. Before dyeing with basic dyes goods must be mordanted with titanium salt, preferably one per cent titanium oxalate.

The method recommended is to drum goods in

1 per cent titanium oxalate
250 per cent water at 100° F.

Drum for 15 minutes, then add half the required amount of basic dye dissolved in one gallon of boiling water, first making the dye into a thin paste with a little boiling water to which is added 100 ccs. of 30 per cent acetic acid. Filter dye solution before adding to the drum. Process for 20 minutes, then add the remainder of dye and continue for another 10 minutes. Make up the acid dye solution by dis-

solving the dye in one gallon of boiling water and filtering. Pour half of the acid dye solution into the exhausted basic dye liquor and drum as usual. Add four per cent sodium acetate dissolved in a small quantity of water and run for 5 minutes before adding the acid, preferably formic—ap-



BOARDING MOVEMENTS FOR HARD GRAIN E.I. GOATS FOR MOROCCO . . .

proximately ¾ lb. for every pound of dye used. At the end of 10 minutes the remainder of the acid dye should be added and drum run for 10 minutes. Take goods out, rinse well in cold water, allow to settle for two or three hours before striking out and straining.

Finishing

Strained goods must be fluffed and brushed; they are then ready for seasoning. It may be that a certain amount of flaming will be necessary to revive the color, but this should be cut down to a minimum. A small percentage of mucilage in the dye solution, about five per cent Irish moss or gum tragacanth, is advisable to prevent uneven absorption of color and to help fill up porous parts of the grain.

The procedure adopted in many modern British tanneries is to spray the goods with a suitable cellulose pigment finish, air off and glaze, soak goods in cold water for a few minutes and allow to sam for eight hours. Next wet grain, dry, spray with a top finish, glaze and reboard. If, however, a dull lustre finish is required, then the second glazing should be omitted. Naturally, this *modus operandus* can be considerably modified and, indeed, in some cases a brushing cellulose dope is used instead of a spray coating, the object being to secure better penetration and to ensure a firmer and more tenacious film for the priming coating. The cellulose dope used for morocco must be one specially made for the work and able to give a highly flexible and strong film. Most upholstery and fancy goods manufacturers prefer either cellulose dopes or the latest acrylic resin dispersions, because of their high resistance to moisture, rubbing and light. On the other hand it has to be admitted that, unless great care is taken, the finished leather is liable to have an artificial appearance which detracts from its natural beauty. For bookbinding purposes the use of cellulose dopes is not so general, the aim being to choose a finish which will not in any way detract from the natural appearance and feel of the leather. Egg albumen seasons suitably modified to give a very elastic film are frequently used for bookbinding leathers.

XXI

RAW KIPS FOR UPPERS

A CONSIDERABLE number of these kips are purchased by tanners specializing in bag, case, saddlery and stout upper leathers. Kips generally average out above 5 lbs. and below 25 lbs. These are usually considered to be the outside limits as those skins below 5 lbs. are classed as calf and those above as hides. Some tanners have a category, namely "light hides," but these are really kips.

Sun dried, arsenicated, dry salted and wet salted E.I. kips are available, but the first named, being the cheapest, are the most common in Europe and, incidentally, the most difficult to deal with with any assurance of success. Common defects in dried goods include "taint," sore shoulder, pox, sunburns or hard patches, warble, ticks, scratches, scabs, butchers' marks and brands. If the skins have not been properly and cleanly flayed this is a serious drawback and entails endless trouble in the tannery. Unless the bulk of the flesh is removed it will prove impossible to carry out successfully any of the preliminary beamhouse processes. It is also worth noting that the presence of patches of flesh causes the skin to buckle and form creases which are sometimes very difficult to remove. Fleshy kips should be soaked in a weak sulphide solution approx. 0.3% for 24 hours and then hand fleshed or broken over the beam before completing the soaking and continuing with other beamhouse proc-

esses. Goods flesh better after alkaline treatment rather than one of an acid nature.

Arsenicated goods are always in a far better condition than sun dried kips, but tanners report a great deal of difference between the various types and sources of supply. The writer is of the opinion that where trouble is met with in the treatment of arsenicated kips it is mainly due to one or more of the following reasons:

1. Skins have been allowed to become tainted before treatment with arsenical solution.
2. The solution is used too sparingly to reduce curing costs.
3. The actual treatment with the preservative is hurried and incomplete.

Dry salting and earth cures are both common methods of preservation, but wet salting is only occasionally met with, although it is a method well able to give extremely good results.

Soaking

The method adopted naturally varies a good deal according to the type and condition of the kips to be handled. For sun dried goods containing only about 10% moisture, the following treatment is recommended:

1. Soak in used soak water, i.e., one through which two packs have passed, for eight hours. Draw and transfer to (2) liquor.
2. Make up a pit with ¼ lb. sodium sulphide per 100 gallons water. Soak for four hours, then draw, plunge up or otherwise agitate liquor and throw back goods. Allow to remain for 48 hrs., then dry drum for ½ hour or, in extreme cases, stock for 25 minutes.

3. Re-soak in weak sulphide solution until soft and workable.

No hard and fast rule can be recommended, but by adopting a procedure similar to the above excellent results can be obtained. In the case of cleanly flayed goods it may not be necessary to drum them as soaking in the sulphide solution will bring about the desirable softening and swelling action; alternatively, if drumming should prove desirable, it could be carried out in the presence of running water, using the lattice door. Dry salted and arsenicated kips require plenty of movement in the soaks and a method recommended by the writer is as follows:

1. Soak in used soak water for 24 hours.
2. Wet drum for four hours.
3. Soak in clean water containing 1/6th lb. of sodium sulphide per 100 gallons water. Draw goods after eight hours and leave in soak until soft and workable.

Wet salted kips should not be soaked in a used soak liquor as all they require is leaving in fresh water until ready for depilation. In the case of tainted goods, which are particularly open to damage by bacterial attack, it is advisable to dispense with old soaks and to add 0.04% zinc chloride to the clean water used (this amount of disinfectant is based on bundled weight of goods).

Depilation

Two methods are readily available for kips. First, the painting method, which results in the economy of the hair. Second, the total immersion method, entailing the destruction of the hair. The former method is recommended for goods to be vegetable tanned and the latter for kips intended to be chrome tanned. Any good depilatory paint, such as

that given for sheep and goatskins, will give equally satisfactory results for kips. Total immersion method of depilation, described in the case of calfskins for box and willow, can be adopted for kips.

Liming

The writer recommends the use of 5% lime and 0.5% sodium sulphide (crystals) on the unhaired weight of goods. Pit liming is the most suitable for kips and a three pit system gives excellent results.

1st Pit (through which two packs have passed).
2nd Pit (through which one pack has passed).
3rd Pit (new liquor).

Goods should have two days in No. 1 with one draw a day, followed by two days in No. 2 with one draw a day. The length of time in the fresh lime varies, but is usually about five days with two draws a day. Variations can be made in the working of the system according to the type of goods being processed. Thus, kips intended to be tanned with vegetable extracts should spend three days in No. 1 pit, followed by three days in No. 2 and four days in No. 3. On the other hand, stock to be chromed can miss No. 1 altogether and after being two days in No. 2, pass straight away into No. 3 and remain for five days. Kips should next be cut down the center, fleshed and split to the required substance.

Deliming

Limed goods must be drummed in running water for ¾ hour, using a polygon drum for preference, then partially delimed in the drum with 1½% boric acid for ¾ hour, washed up and bated.

Bating Kips for Vegetable Tanning

This must be more thorough than is the case for goods intended to be chrome tanned. Method recommended is to bate stock in paddles containing 1% good enzymic bate, such as Cutrilin G.G., at 95 deg. F. for 1¼ hours, or until goods are nicely fallen. The proportion of bate used is calculated on the limed and fleshed weight of the kips and it should be added to a used bate liquor. The writer considers it advisable to run the goods in the used liquor for five minutes without adding the fresh bate and then to add this mixed into a paste with a little warm water. After bating it is advisable to drum or paddle the goods in running water for 10 minutes. They can then be pickled. Some tanners scud the goods after bating and where the extra cost can be allowed this is to be heartily recommended.

Bating Kips for Chrome Tanning

Good results may be obtained by bating for 45 minutes with ¾% enzymatic bate on limed weight at a temperature of 95 deg. F. The paddle is the best vessel in which to carry out bating, as greater control of the process can then be maintained. After bating, the goods may be scudded and drummed in running cold water for one-half hour before pickling.

Pickling

This is best carried out in a drum, using 2½% sulphuric acid and 20% salt in 150% cold water. Drum for 30 minutes for kips to be chromed and 20 minutes for goods to be vegetable tanned.

Vegetable Tanning

Naturally, different tanners vary a good deal in their views regarding the most suitable blend of tannins for kips, but the following combinations can be recommended:

Chestnut	Hemlock	Quebracho
Quebracho	Chestnut	Myrobalans
Oakwood	Myrobalans	Valonia
		Sumach

A method which the writer knows capable of giving good results consists of drumming the goods in a spent tanning liquor to start with, containing 5% iron free synthetic tannin and 5% salt. After two hours running, the syntan can be increased to 10% and goods drummed for a further two and one-half hours. The drum should then be allowed to remain stationary until next day, when the kips can be taken out and thrown into a freshly made liquor built up of a suitable blend of extracts, such as chestnut, quebracho and oakwood. This should give a nice firm tannage suitable for case leathers. By replacing myrobalans for the oakwood and the hemlock for the quebracho it is possible to make a very good blend and the tanned leather is particularly suitable for uppers. This leather lends itself very well to semi-chroming. The third recipe gives a clean, firm leather for general purposes, but specially fitted for currying. By running the green goods in synthetic tannin first the grain is tightened up and any tendency to looseness in the flanks removed. The color of the finished leather is also improved. After tanning in the drum the goods should be horsed up and allowed to samm for at least eight hours. It is a good plan to lay heavy kips away in sumach for 12 hours before

samming, but tanners seldom do this as they do not think the time or cost is justified.

After setting by machine the kips must be oiled off with a mixture of degras and neatsfoot oil, using one part neatsfoot to one-half part degras. Dry under natural conditions. It is worth noting that some tanners favor the use of wattle bark extract towards the end of the tannage in which hemlock or quebracho is the main tannin employed.

Chrome Tanning Kips

The procedure recommended should follow that laid down for box and willow calf as the tanner's aim is to produce a leather closely resembling this. After tanning with a suitable basic chrome compound, the goods should be well washed in running water in a drum with a lattice door and then drummed with 5% of a suitable syntan, temperature 95 deg. F., using 150% water, amounts being based on the pickled weights of goods. The object of this after-treatment is to tighten up the grain of the leather and so improve its general appearance. If the right type of syntan is employed it also serves to improve the handle by helping to fill out empty flanks. After drumming in the syntan the goods should be sammed for several hours, then struck out ready for dyeing in the usual way. For box it is recommended to use 1¼% hematine and ¼% sumach extract, whereas for willow about 1½% gambier and ½% sumach extract will be found quite suitable. A suitable fat liquor is as follows:

1% Sulphonated cod oil
1¼% degras
1% neutral soap flakes

First dissolve the soap flakes in five gallons of hot water, then add the sulphonated cod and degras; emulsify thoroughly. Add the warm emulsion (110 deg. F.) to ¾ of

the exhausted dye liquor and drum for ½ to ¾ hour. An alternative recipe is 1½% sulphonated cod; 1½% sperm oil and ½% soap flakes. Some tanners prefer the latter recipe for box as it gives a better fed leather. After dyeing and fat-liquoring, the goods should be glycerined on the machine, using a solution made up of one part glycerine and three parts water. Allow goods to samm for four to six hours and then dry. The procedure following should be the same as for box and willow.

Fat Liquoring
Vegetable Tanned Kips

The writer considers that the best results are obtained without the use of soap. Emulsions made up of sulphonated cod oil and degras, using 1½% of the former and 1% degras, will give a satisfactory, well nourished handle to the leather.

Semi-Chrome Kips for Uppers

This is a line very popular with British shoe manufacturers. A method of production carried out in one important tannery is as follows:

Goods are partially tanned in a mixture of quebracho and myrobalans, then washed up and hydro-extracted to remove excess of water and loose tannin. They are next drum tanned in a basic chrome liquor, washed and processed in a 3% solution of a suitable syntan to plump up loose flanks and tighten the grain. Next follows washing, neutralization with borax, washing, mordanting and dyeing with acid dyes in the usual way. This type of leather benefits from the use of a substitute egg yolk fat liquor with sulphonated cod and sperm oil. Suitable recipe is:

1¼% substitute egg yolk
1½% sulphonated cod
¾% soap flakes

Development of the above process can prove very economical and the leather is hardwearing, reasonably waterproof and possessing a good appearance.

Kips for Printing

Crust stock should be slit down the back preparatory to soaking in water. Next follows band knife splitting and shaving. Goods should be stripped with 2% borax, temperature of water 95 deg. F., for 25 minutes. Afterwards they must be thoroughly washed in running cold water and cleared with ½% sulphuric acid on crust weight, for 15 minutes, followed by washing and re-tanning. The latter process is best carried out with:

7% gambier
6% quebracho (sulphited)
1% salt

If a very light colored leather is required, then it is advisable to substitute a good bleaching syntan for the gambier. Another good recipe makes use of:

5% sumach extract
5% myrobalans
3% quebracho or wattle

After tanning, goods should be allowed to samm and then be struck out ready for dyeing. Acid dyes must be employed for good penetration. Fat liquor with:

2% sulphonated cod oil
1% sperm oil

Strike out, samm, set out and then toggle up or strain lightly. When dry, sawdust and then stake lightly, taking care not to get the stock "boggy." Some tanners next buff

the goods on the grain so as to obtain a perfectly level surface, but the writer considers that this should be avoided unless the grain is obviously imperfect. Next brush the grain surface, flame if necessary, air off and apply pigment finish suitably thinned down. Air off and then print, spray on clear glazing season, dry, glaze and finally iron. It is possible to obtain many striking effects by altering method of procedure. Thus, after printing, a spirit solution of basic dye can be brushed or sprayed on to obtain realistic coloring. Alternatively, a very light colored dope may be applied as a bottom and a dark colored glazing finish sprayed on after printing. Either casein bound or cellulose dopes can be used, but the former are cheaper and more versatile. A simple glazing season recipe is:

½ lb. egg albumen
1¾ oz. suitable acid dye
⅞ pint milk
1 gallon pigment finish
4 gallons water (soft)

The addition of 2 oz. glycerine is recommended by some tanners, but the writer considers that good results may be achieved without it. If the color is dark a little bullock's blood will help matters and improve the glaze, about 4–5 fluid ounces are sufficient for the above quantity of season.

White Chrome Calf or Kips

The following method is recommended:

Drum the chrome tanned stock in running cold water for one and one-half hours. Drain or lightly hydro-extract and allow goods to settle. Shave and wash up in water 120 deg. F. for 30 minutes. Run off a good proportion of the water until only just sufficient is present for the goods to work about in without risk of heating. Add 10% bleaching syntan

and drum for one and one-quarter hours. If possible, allow stock to remain in the liquor overnight. Next day wash in running water for one-half hour, drain or hydro-extract and then transfer to the pigment solution. This can best be made up with:

5% titanium oxide
2½% sulphonated neatsfoot oil
25% water at 125 deg. F.

Drum for 45 minutes and then add:

2% titanium oxide
½% sulphonated castor oil

Continue drumming for 20 minutes. Drain goods.

If desired, a small amount of suitable dye may be added to the pigment solution 10 minutes before conclusion.

When dry, the stock can be finished with cellulose or casein bound dopes in the usual way.

The above recipe is capable of producing a permanent non-dusting white leather, but a better white can be obtained by use of a method which employs barium chloride and sodium sulphate. After drumming stock in the bleaching syntan, process goods in:

5% barium chloride
50% water at 120 deg. F.

Run for 15 minutes. Drain and transfer to a drum containing 5% sodium sulphate and 50% water at the same temperature. Drum for 15 minutes. Wash in running water for one hour and, after draining, proceed as in the first recipe.

XXII

LAMBSKINS FOR GLOVING

LAMBSKINS for gloving purposes must be very carefully chosen. The pelts should be of even texture, free from surface blemishes such as scars, cuts, cockle, etc.; well nourished but not greasy or showing signs of loose grain. All skins should be of a uniform shape so that the minimum amount of waste is incurred when cutting up in the workshops. Unless goods are properly sorted in the lime sheds there will inevitably be a cause for needless complaint when they reach the warehouse. It is advisable, therefore, to sort the pelts from the fellmonger and then to resort the packs after fleshing when practically all defects should be quite obvious.

LIMING

On arrival at the tanners the goods should be sorted, as explained above, then thrown into a mellow lime; that is, one which has been used not more than four times and not less than twice. If goods are to be paddled and not limed in pits, then the first processing should take place in a liquor through which three packs have previously passed. This preliminary liming is most important as it prepares the fibres for more extensive treatment in the new lime and also achieves to a very useful degree something of the action of a bate. The experienced tanner knows that a prop-

erly limed pelt always comes down quicker and to a better degree in the bate than a pelt which has been hurriedly limed.

Some tanners give all fellmongered goods a short wash-up in cold water before liming takes place, but in the writer's opinion this is inadvisable as it tends to swell the goods too early in the process and also leaves the grain rather harsh. The best procedure is to process goods in a used or mellow lime for three days giving two draws a day in the case of pit liming. For paddle work it should only be necessary to run the paddle for half an hour a day; not more. Afterwards see that all pelts are poked under the surface of the liquor.

At the end of the allotted period remove the goods from the liquor and spread them out on a clean floor in the form of small piles, taking particular care to see that all pelts are smoothed out and that no creases are allowed to become set and to cause definite marks through the effects of pressure. This is a precaution which only experience really teaches. Cover the piles over with large sheets of sacking soaked in lime liquor and leave the pelts to settle for 24 hours, or at least 12 hours. This period may be considered by some tanners to be sheer waste of time, but in the writer's opinion it achieves a most valuable purpose. The fibres absorb a good deal of liquor and thin flanks tend to gain in weight and there is a general leveling-up of substance, all of which is very desirable.

Next the goods require a more complete liming. If time does not permit, the goods may be passed straight away into a lime and sulphide solution, but it is far better to give the pack a couple of days in a liquor through which only one pack has passed. A lime and sulphide mixture gives better results than either a straight lime or a sulphide. Instead of ordinary sodium sulphide use may be made of the

more recent sodium sulphydrate. It is claimed that the use of this milder alkali avoids damage sometimes caused by excess alkalinity and permits production of a stronger, clearer leather with a better and smoother grain. Tanners who have so far tried out this comparatively new chemical report that it is far less trouble to use than sodium sulphide and facilitates quicker and more effective removal of pigment and filth during scudding.

For an average pit, a total of approximately 120 lbs. hydrated or slaked lime and 10 lbs. sodium sulphide or sulphydrate will be found sufficient. It is advisable to use only half of the sulphide at the commencement of the process, the remainder being divided into three equal portions, one of which should be added to the liquor, after removing goods, each day. This method tends to produce a better kind of pelt than would result from the use of maximum alkalinity at the commencement. It is recommended to use either hydrated lime or to slake lime and sieve it before use. This prevents any possibility of lime burns which cause serious damage to goods.

As regards length of time, at least seven days for pit liming and four for paddle liming are necessary, but no hard and fast rule can be laid down. In warm climates and in very hot weather the time can be reduced so as to compensate for the extra swelling which occurs when the chill is taken off the water. One draw a day is necessary for pit liming and half an hour's paddle work for paddle liming. At the end of the liming process the goods should be laid out in heaps, preferably slicked or smoothed out to remove creases, and left for 24 hours.

After liming, the goods should be trimmed and cobbed, that is, all traces of wool removed by means of a blunt unhairing knife. Next the pelts need to be fleshed so as to remove all traces of flesh and fat, but care must be taken to

avoid eating into the actual substance of the skin by close setting of the rollers. Goods must next be soaked in warm water, 90° F., for 10 minutes and well scudded, preferably by hand over a beam, otherwise machine scudding should be carried out twice.

The importance of scudding cannot be over stated as it not only removes all filth and pigment thus insuring a clear, clean grain in the finished leather, but also removes a good deal of grease. If most of the grease is removed during beam house operations it greatly facilitates operations at a later stage of the processing. The addition of 2.5 per cent borax to the water used for soaking the pelts before scudding is recommended by some tanners who claim that it helps considerably in the removal of natural grease. The borax not only saponifies a certain amount of grease but also emulsifies the fat. Thorough scudding after liming should never be omitted simply because a later scudding after bating is undertaken. The second operation really complements the first.

Deliming

Goods require thorough washing in a drum, using the lattice door and plenty of cold water. Half an hour is usually sufficient for this preliminary washing. Instead of employing one of the recognized deliming agents it is preferable to make use of a sour bran drench which gives the grain a finer break and is more suitable for gloving leather than either a straight acid or alkali bath. After deliming in the paddle, wash the goods thoroughly in cold water ready for bating. The addition of lactic acid to the sour bran is recommended. A good formula is 60 lbs. bran to 100 gals. water to which can be added ¾ pt. of lactic acid. Goods should be paddled.

Bating

The most suitable bate for glove leather is dog dung, but most tanners prefer to use a modern enzymatic preparation because it is more convenient in use, more hygienic and generally the process is easier to control. In any case dog dung is now difficult to obtain in regular and uniform quantities.

A good method of bating consists in running the goods in a liquor which has been used once, temperature 90° F., for fifteen minutes. The paddle is the most suitable vessel for the purpose. At the end of the above period add from 1¾ to 2½ per cent fresh bate and continue working until the goods have fallen to the degree required. The foreman in charge should be able to tell immediately whether the skins are properly bated and the process must be very carefully supervised so as to insure that it is stopped at just the right moment.

Too little bating means that the finished leather will be too tight on the grain and lack that elasticity and stretch so necessary for first class gloving leather. On the other hand, too much bating will cause the leather to be tender and cloth-like.

It is well to realize that the success of the bating operation not only depends on the actual degree of processing, but also on the satisfactory completion of the previous deliming. The pH of the goods must be within fairly narrow limits of alkalinity, that is, about eight to nine. For this reason it is preferable to use a very mild deliming agent such as a sour drench; checking the degree of deliming by means of a suitable indicator such as phenolphthalein.

After bating, wash up the goods in a paddle containing warm water, 90° F., for 10 minutes, then scud by hand,

or if a machine is used run the goods through twice. Thorough scudding is absolutely essential after bating as it removes a great deal of emulsified fat as well as filth and pigment.

Pickling

There is a good deal of difference of opinion among tanners regarding the advisability or otherwise of pickling goods for gloving. Some tanners maintain that it tightens up the leather too much and tends to make the grain give when closely stitched. On the other hand, others affirm that it is a definite advantage for the following reasons:

(1). Improves the handle.

(2). Enables goods to be stored for indefinite periods.

(3). Enables goods to be sorted more accurately than is possible in the lime sheds.

(4). Facilitates degreasing in the wet condition.

These considerations are important and in the writer's opinion swing balance in favor of pickling.

The pickling can be carried out in either drum or paddle. Suitable proportions of acid and salt are 3 per cent sulphuric acid, D.O.V., and 13 per cent common salt and 120 per cent cold water per 100 lbs. bated goods. Run the goods in the brine containing two per cent acid for 30 minutes, then add the additional one per cent properly diluted and run for a further 15 minutes.

At the end of this period in the drum, the cut surface of the skins should be colorless to phenolphthalein and have a pH of approximately 2. After pickling, always allow the goods to be stacked or horsed up for half an hour before attempting to sort them. If it is required to build up a stock of pickled pelts and keep them for longer than a month, it is advisable to give them a brine bath using a

fully saturated solution. All that is necessary is to soak the skins in the liquor in a large vat or paddle for 40 minutes, then drain goods for 12 hours before making them up into dozens.

Degreasing

As far as possible it is strongly advisable to carry out degreasing before tanning as it is not so exhaustive and has no undesirable weakening effect on the leather. Petroleum degreasing, although very necessary in certain cases, frequently has a slight hardening effect on the grain of the leather and tends to make it crack when subjected to severe strain such as is occasioned by constant flexing when gloves are in use. All that is really necessary in wet degreasing is to remove the surplus grease which would otherwise cause discoloration of the grain.

The author considers the following method very suitable for glove leather and it can be applied with equal success to both sheep and goatskins.

For 400 lbs. pickled pelt use approximately 14 gals. of kerosene in a drum, running it for one hour and 15 minutes. Next pour in 30 gals. of a five per cent salt solution, temperature 92° F., and drum for 20 minutes. Take out goods and wash in warm water, 93° F., for 15 minutes. The addition of a small proportion of a surface active chemical to the wash water, such as a sulphated alcohol and sulphonated oil is helpful in emulsifying any grease present on the grain or flesh of the skin. There are a number of excellent proprietary wet degreasing agents on the market which can be thoroughly recommended for use either alone or in conjunction with a fat solvent. If desired, goods can be pressed in a hydraulic press before carrying out any wet degreasing process, or the latter may be omitted.

Depickling for Alum Tannage

This is necessary in the case of all goods to be alum tanned. There are various methods of depickling and claims are made for each one by tanners. In the writer's opinion Payne's method gives the most uniform results. The formula has been given before in this series but will bear repeating.

Ammonium sulphate	4 lbs.
Sodium chloride	10 lbs.
Sodium bicarbonate	3 lbs.

The process is best carried out as follows: Weigh out the above chemicals and dissolve them in 40 gals. of water in a drum; temperature, 100° F. Run the drum for a few minutes until the temperature has dropped to 95° F. The above liquor should be enough for about 20 dozen skins, depending on the size. Usual time of processing is half an hour but this is by no means fixed and length of process should be influenced by reaction of cut surface of pelt to phenolphthalein or other suitable indicator.

Depickling should be carried on until the pH of the skin is approximately 5. Again opinion differs about this, but the above answers quite well. After pickling goods should always be well washed in cold running water for 10 minutes and then tanned straight away.

Alum Tanning for Gloving Leather

A very simple method is the following:

20 lbs. alum
10 lbs. salt
40 gals. water

(Sufficient for 20–25 dozen lambskins.)

Dissolve the alum in water at 200° F. and then stir in the salt. Use about 10 gals. of water in which to dissolve the alum and salt and then add this strong liquor to 30 gals. of cold water in the drum; total of 40 gals. Temperature of processing liquor should be about 80° F. Run goods in this liquor for one hour and then leave for 12 hours in the stationary solution. Horse them up and allow to drain for a further 12 to 24 hours. This is most important as it helps to fix the tan and insures that the leather will be properly tanned.

Do not throw away the alum liquor but run off 10 gals. in a tub. To the remainder of the liquor which is still in the drum add 10 lbs. flour, five lbs. oatmeal, one pt. neatsfoot oil, and 1½ pts. of good egg yolk. Drum for 1¼ hours and then take out goods and allow them to drain on horses for eight hours before drying in an open shed. When dry, stock the leather away for a week so that it can age.

It is a great mistake to try and hurry alum tanning, but if it is absolutely essential that the goods should be tanned as quickly as possible then it is advisable to add eight lbs. hyposulphite of soda dissolved in five gals. hot water to the alum liquor after drumming the goods for ½ hour. This fixes the tannage fairly rapidly but has the disadvantage that it leaves the flanks somewhat thin and extra feeding may be necessary.

When properly aged the goods usually require further feeding and this can be done quite simply in the following manner:

Throw the skins into a drum containing only a small amount of water, 95° F., usually 20 gals. for a pack of 25 doz., and drum for five minutes. Add 10 lbs. flour, five lbs. oatmeal, three pts. sulphonated neatsfoot oil, one pint egg yolk substitute and five lbs. china clay. Drum for ¾ hour. Horse up goods and dry out in a warm stove.

The liquor remaining in the drum should be saved and used as the basis for a new fatliquor, the proportions of the fatliquoring ingredients being reduced by one-third. When dry the goods should be aged for 24 hours in a damp or cold shed, then seasoned with a clean damp sawdust or by merely sprinkling with water. Next they should be well staked and strained on boards.

Final processes consist of staking or stoning and buffing. To improve the appearance of the grain the goods can be lightly pressed in a cold press or ironed with a warm but not hot iron.

Lambskins for Chrome Tanned Gloving Leather

Both the single and double bath method give good results but the writer prefers a combination of alum and chrome tannage. Drum the goods in the following solution:

$$\left.\begin{array}{l} 12 \text{ lbs. alum} \\ \ \ 6 \text{ lbs. salt} \\ 30 \text{ gals. water} \end{array}\right\} \text{(20 dozen lambskins.)}$$

After ¾ hour drumming add 10 lbs, flour and continue drumming for another 20 minutes. Dry goods in a warm shed, 85° F., and if possible age the skins for a few days before continuing with the retanning process.

A good proprietary single bath chrome liquor is recommended for retannage but equally good results may, of course, be obtained by use of chrome alum or a factory chrome liquor. The alum tanned goods should be drummed first in just a little warm water, temperature 92° F., so as to soften them. The chrome tannage can then proceed in the usual way. Thorough neutralization is essential and borax is the most suitable agent for this purpose. Approximately 1¾ per cent borax on the pickled weight of goods is advisable. After neutralization all traces of free mineral salts

should be removed by washing in running cold water for half an hour.

Goods may then be mordanted with two per cent gambier and 1½ per cent sumach extract for ¾ hour. Dyeing is best carried out with acid colors, taking particular care to insure maximum fastness to rubbing. Fatliquoring with a blend of sulphonated neatsfoot and egg yolk is strongly recommended.

A good formula consists of six per cent sulphonated neatsfoot oil; 2½ per cent egg yolk substitute, and 1½ per cent sulphonated cod liver oil. The addition of a small proportion of sulphated alcohol or other soap substitute to the extent of ¼ per cent is useful as it increases the penetrative powers of the fatliquor emulsion. Some tanners consider that soap is necessary and the writer agrees that 1½–2 per cent good curd soap is a useful additive to any chrome fatliquor. Optimum temperature for fatliquoring is 115° F.

Fat liquoring can be carried out either before or after dyeing. The advantage of the former is that there is very little stripping action on the leather, but at the same time the penetration of the dye is not so good. If the fatliquoring is carried out after dyeing there is no reason why excellent results should not be obtained and, as mentioned previously, it is probable that a better degree of penetration will be obtained so that the finished gloving leather will not show a light bottom when stretched.

The use of one per cent ammonia tends to increase the fastness of the dye and it is a good plan to drum the goods in this before adding the dyestuff. Towards the latter stages of dyeing the addition of 1½ per cent of sodium acetate is recommended as it greatly improves the handle of the finished leather.

If the dyeing has been properly carried out there should be very little need for any finishing, unless, perhaps, a small

degree of wax finishing is given. After dyeing, goods must be well washed, then horsed up to drain, struck out, dried, and finally conditioned in damp sawdust ready for staking. Next the goods are buffed, restaked and stoned. Final operation is polishing on a plush wheel followed by brushing.

Goatskins for Gloving

In general the practical notes dealing with lambskins apply equally well to goatskins. For fatliquoring a greater proportion of ingredients is essential, usually 15–20 per cent more than is normally necessary for lambskins. Drying temperature can also be safely increased to 125° F. provided goods are properly conditioned before staking.

XXIII

EAST INDIA KIPS

East India tanned kips are favorites among English tanners for sports goods, particularly footballs and certain types of sports footwear. Goods likely to prove the most serviceable for this specialized work are those free from obvious mechanical damage likely to weaken materially the actual structure of the protein. The sorter should, therefore, carefully assess the degree of damage due to flay marks, barbed wire scratches, currycomb, goad marks, thorn scratches, brand marks and reject those skins which show an obviously restricted cutting area. Such goods may find other uses where the standards are not likely to be so high. Damage due to disease may not, at first, appear so obvious as that caused by mechanical damage, but nevertheless where the skin is wasted by disease or insect pests it is very hazardous to utilize the weakened leather for sports goods which require a very high tensile strength and resistance to wear.

It is as well to stress the fact that defects never diminish in seriousness during processing, although they may become less obvious due to clever dyeing and finishing. Thus inherent sources of weakness shown in the crust should be regarded with suspicion and their effect on the ultimate value and usefulness of the leather rightly judged. Damage due to some diseases or pests is often difficult to assess. Thus follicular mange often causes a kind of insidious wasting

which may not appear to be very serious and yet during the process of manufacture might easily cause holes to appear and make drastic encroaches on the actual cutting surface. On the other hand, damage due to ticks, usually quite easy to trace, is frequently not serious enough to merit the rejection of the goods. Everything depends on the judgment of the sorter and the more experienced he is, the better equipped he will be to exercise that nice discrimination so important to the interests of the tanner.

Parcels of goods selected for processing should be trimmed and weighed before wetting down and stripping. The former is best carried out as follows:

(1) Goods should be soaked in cold water in paddles or vats for eight hours. The pack or pile of kips can be kept immersed in the water for the required period of time by placing planks of wood on top of the heap and weighing them down by stones.

(2) It is a good plan to soak the kips in cold water as above before drumming, but, if absolutely necessary, the preliminary soaking can be dispensed with. Drum work using water at 100° F. should be carried out for ¾ hr. or until the goods are thoroughly softened. In the case of very obstinate leathers the use of wetting-down agents is recommended.

After soaking and softening the kips can be hydroextracted, lightly set and then piled up in heaps for four to eight hours before splitting on the bandknife machine. Very great attention should be paid to the condition of the goods before splitting otherwise this process will be difficult to complete successfully.

Stripping

A mixture of borax and soft soap gives better results than the use of just one alkali. Recommended proportions are:

1½% borax
1½% soft soap
300% water at 100° F.

Time required for stripping depends on the amount of unfixed tannin, soluble mineral salts and surface grease present, but usually about half an hour is sufficient to remove all that is necessary.

Washing

After stripping the goods must be well washed in running cold water. This can, of course, be undertaken in the same drum; merely putting on a lattice door and removing all bungs. A period of at least 20 minutes is necessary to get rid of all traces of soluble materials.

Clearing

It might well be asked, is this process absolutely essential? Many tanners believe that it can be omitted with a saving in material, labor and time. On the other hand, it should be remembered that clearing does effect a considerable improvement in color and by reducing the pH of the leather facilitate the penetration and even absorption of the basic chrome salts. Altogether the writer considers the process to be definitely useful.

The simplest clearing agent is sulphuric acid, about ¼% is sufficient, diluting it with approximately 400% water at normal temperature and processing for half an hour.

Chrome Tanning

Any good one bath proprietary tan liquor will give excellent results provided the basicity is approximately 85 and chrome content 130. It is advisable to carry out tanning in a drum and to commence by running the goods for five min-

utes in a weak saline solution, about three per cent sodium chloride or sulphate; the character of the salt depending on the nature of the basic chrome salt employed.

Strong batch liquor is run into the drum in three portions at intervals of ½ hour, ¾ hour and 1¼ hours. Total retanning time, using 150% water, should be approximately three hours, but may be more if penetration is not satisfactory. Goods should be left immersed in the liquor overnight, then next morning drained, lightly hydro-extracted and washed up preparatory to neutralization.

Washing is best undertaken by drumming in running water for ½ hour followed by neutralizing with 1¼% borax for ¾ hr. and rewashing in cold running water for the same period of time. Some tanners make the mistake of continuing the washing for too long a period so that the leather is left somewhat impoverished.

When neutral, the goods can be set out ready for dyeing. This may be carried out with coal tar dyestuffs or mordants. In any case, due regard must be paid to subsequent running of the colors during stuffing or fat-liquoring. Some tanners dye or stain the goods after stuffing, but the reverse of this is generally easier and invariably quite successful. As only tan or very light shades are required for sports goods, a run in titanium salt followed by a tannin solution, such as sumach extract or gambier, generally gives good results. Where it is possible to obtain the required color without the use of coal tar dyestuffs, then this is recommended. There is no need to describe the dyeing operation as this follows the normal procedure previously described by the author.

Fats for Stuffing

Those most generally suitable for this class of work are tallow, cod, sperm and mineral oils. Choice has to be influenced by the following important factors:

(1) Suitability of fats for particular purpose in mind. For instance, where it is desired to produce a soft, very well fed leather then the use of sulphonated oil or neatsfoot oil, perhaps both, is recommended. Paraffin waxes and also some of the modern synthetic waxes are very useful for stiffening purposes, but they have to be employed with a certain amount of care otherwise there will be too much danger of crystallization.

The important point to bear in mind is that if a high degree of suppleness in the finished leather is required, then the melting point of the stuffing grease must be sufficiently low to permit this. Great attention must, indeed, be paid to this question of melting point as if it is not adjusted correctly the finished leather will lack those characteristics, particularly a clean dry appearance, so essential for the sales appeal of the manufactured goods.

In the preparation of the stuffing grease, the incorporation of a little emulsifying agent, such as a good cyclohexane soap, is a definite advantage, although very few tanners take the trouble to use anything of the kind. A minimum of two and maximum of five per cent of the emulsifying agent will produce a marked improvement in the rate of absorption of grease and the even penetration of the grease throughout the area of the leather.

(2) Economics of stuffing process, which means that obviously expensive fats cannot be used for cheap lines. In most cases it is possible to dispense with degras and to increase the proportion of mineral greases to save sperm or other natural fats.

(3) Ability of fats and waxes to resist spueing or crystallization on the grain of the leather. This means that careful adjustment of the cod oil content of the grease must be made; cod oil being the chief spue offender.

In connection with the prevention of crystallization and

spue of stuffing greases, the writer considers that the use of special chemicals or "inhibitors" might be worthy of attention. Such chemicals as are used in the oil industry for delaying or inhibiting wax crystallization are of considerable potential interest to tanners. Whitmore (Organic Chemistry) mentions that such substances consist of complex mixtures of complicated molecules incapable of crystallization. They are, in all probability, absorbed on the first micro-crystals and prevent their growth and action as nuclei for the crystallization of the main mass of wax.

Stuffing

Chrome tanned leather should be hydro-extracted so as to reduce the water content to the minimum before stuffing. Percentage of water present in the leather has a considerable influence on the degree and rate of fat absorption. It is no use giving an empirical figure for this as the tanner must vary it according to the peculiar conditions required by his sales organization. The best practice is to hydro-extract goods, then set. Afterwards goods should be hung up in a drying loft until they are nicely sammed, then placed in piles to season before continuing with the actual stuffing operation.

To facilitate absorption of fat, sometimes difficult in the case of coarse emulsions, goods should be given a preliminary treatment with a suitable wetting agent. There are many excellent proprietary agents available and one or other can be employed just prior to hydro-extracting and immediately after neutralization and washing. The writer has experimented with solutions of urea and this chemical appears to be of service in rendering goods peculiarly acceptable to the penetration of grease and the lightening of the color of the impregnated leather.

After drum stuffing for the required length of time the goods should be taken out and hung up to cool off and dry under open air conditions in a loft with all louvres wide open. Next follows setting. This is best prefaced by a quick dip in hot water, 130° F. Goods may then be set to the best advantage and then dried out in the usual way in a stove at medium temperature.

Dry leather is seasoned in moist sawdust, strained, staked and stoned. Afterwards well dusted with chalk, brushed, rolled and measured. Very often the leather is boarded or machine grained as there is a growing demand for this grade, particularly for special sports footwear.

East India Kips

On arrival at the tannery from the docks or warehouses East India Kips should be carefully sorted and weighed. They must next be soaked in warm water, 95° F., in a large wooden tank for 15 minutes, then stacked in small piles for 30 minutes, followed by drumming in a small volume of warm water, 95° F., for 15 minutes, when they should be nice and pliable and in excellent condition for splitting if this is desired. Most tanners prefer to let the goods sam for a few hours before splitting and it is important that when the leather meets the knife it should cut sweetly and truly. Before splitting most of the large kips are cut in two for convenience of handling.

After splitting, the goods require stripping with either 1½ per cent soft soap or two per cent borax, using water at 100° F. Twenty minutes' drumming will generally be found sufficient to remove the bulk of the loose tannin and filth. Washing in plenty of running cold water is necessary to remove all traces of alkali and organic matter brought into the solution by the stripping agent. If goods are to be re-

tanned with vegetable materials it is desirable to brighten up the color by clearing the goods with ½ per cent sulphuric acid on the crust weight, or ¾ per cent formic, preferably the latter. If, however, the kips are to be semi-chromed, then there is no necessity to clear; all that is required is to wash the goods as thoroughly as possible. Goods to be retanned with synthetic tanning agents can also be safely worked after rinsing and without clearing.

Retanning (Vegetable)

It is obvious that choice of any particular tannin or group of tannin is largely determined by the cost. Thus, sumach or gambier, both relatively expensive materials, must be employed rather sparingly and greater use made of quebracho, hemlock, myrobalans and other economical tannins. A blend of tannins always gives better results than a single material. The following mixture is particularly suitable for kips intended for cheap uppers.

8% quebracho
4% hemlock
2% myrobalans
2% chestnut.

Drum goods for an hour, temperature of liquor 95° F., and then add five per cent sumach and continue for half an hour. Wash goods up in cold water and next horse up and allow to drain for eight hours before setting. The addition of one per cent light mineral oil and three per cent sulphonated codliver oil to the tanning liquor, immediately after adding the sumach, is recommended so as to give the leather a good handle.

Vegetable tanned kips are either stained on the table or drum dyed. Taking the former method first, the procedure

recommended is to oil off goods from the setting machine, using only a very small amount of light mineral oil. Dry goods out in an open shed or under conditions as near to normal as possible. When dry, stake and stain with an acid dyestuff and top off with a basic color dissolved in water containing 10 per cent methylated spirits and one per cent glacial acetic acid. It is recommended to give the grain a coating of mucilaginous matter, ¼ lb. gum tragacanth per gallon of water. This should then be followed by a solution of titanium mordant, so as to obtain the maximum degree of penetration and to ensure even coloring. If goods are to be printed this can either be done after setting or, preferably, after receiving the first or priming coat of stain. The latter course insures that the finished leather will not have a patchy appearance as it is difficult to insure even penetration of dye when a heavily printed and, therefore, irregular surface is stained. It is advisable to apply the first few coatings of acid stain with a stiff brush on the table, but the basic dye can be sprayed on and excellent results obtained. After staining, goods should be aired off, when they will be ready for finishing. The type of finish used must necessarily be influenced by the calls of the shoe factory, but cellulose finishes are now being generally preferred for many classes of upper leather.

Semi-Chrome Retanning

Goods should be washed and stripped, well rinsed and then drummed for 10 minutes in a five per cent salt solution. A suitable proprietary chrome solution, preferably a chrome sulphate, can then be added and goods processed in the usual way as previously explained in the case of semi-chrome sheep.

Drum Dyeing Kips

In the case of goods to be drum dyed, and practically all semi-chromed kips are colored this way, it is advisable to fat-liquor after dyeing and not at the end of the retanning process. Acid dyes are the most suitable and straightforward and the fat liquor should be a neutral solution of sulphonated codliver oil or an efficient egg yolk substitute containing lecithin. Approx. 3½ per cent sulphonated codliver oil or three per cent of the egg yolk substitute in three-quarters of the exhausted dye liquor can be relied upon to give good results. The temperature must be not less than 110° F. and the period of drumming 30 minutes.

Finishing

Semi-chrome kips are usually finished in the same way as chrome calf for uppers.

Kip Linings

The goods are first sorted, then soaked in warm water, 95° F., for a few minutes or until the leather is thoroughly permeated with water. The kips should then be allowed to sam until in just the right condition for shaving or splitting to the required substance required for shoe linings. Stripping is generally unnecessary, but the goods must be properly cleared in order to remove iron stains caused by shaving or splitting. The procedure recommended is as follows:—Tanned kips are taken from the splitting or shaving shop and well washed in cold running water in a large drum provided with a lattice door and with all the bungs knocked out. Usually about ½ to ¾ hour is required in order to remove the bulk of the loose tannin and loading materials usually

present in E. I. tanned kips. After washing, the goods may be lightly hydro-extracted and then drummed in a dilute solution of sulphuric acid; about ½ per cent on the weight of goods is recommended. A small amount of color, acid dye in the form of a concentrated, filtered solution, may be added at the end of the clearing operation if it is desired to tint the leather. Bleached effects are best produced by adding 2–3 per cent of a suitable synthetic tannin bleaching agent to the clearing bath after running goods half an hour or so. Kips should be horsed up overnight and next morning fat liquored with the following solution:

2% textile flakes
2½% degras
1½% codliver oil

Make this up into a fine emulsion by means of a proper emulsifier and process goods at 110° F. for ½ hour. Horse up overnight and next day set out by machine and oil off with light mineral oil. Dry under natural or as near natural conditions as can be obtained and then grain by hand or machine, roll, dust with French chalk and brush. If a smooth finish is required goods should be well rolled or cold pressed, dusted with French chalk and then machine brushed.

Naturally, the above process can be adapted to meet the special requirements of the shoe factory, but it must be very simple and inexpensive as linings are amongst the cheapest and most competitively priced leathers. Where price will allow, it is recommended to give the leather a spray of clear finish or binder before graining and rolling, etc. This greatly improves the appearance of the leather.

Roller Leather

The pelts chosen for this type of leather must be firm in texture; free from all wrinkles; excessive fat; grain defects,

such as barbed wire scratches, sores, cockle insect damage, etc., and of medium weight and square, well proportioned shape. Lambskins from various sources are used for the production of roller leather, but English tanners prefer Welsh mountain sheepskins which are fairly small in size yet of good shape and possessing a fine, clear grain. The importance of choosing the right type of pelt cannot be over emphasized since, when unsuitable goods are put into work it means a large percentage of rejects in the finished warehouse, and this, of course, represents a loss of money, time and labor. Mountain sheepskins are very similar to Persian or E. I. sheepskins and when finished have an exceedingly smooth grain which is ideal for cotton spinning rollers.

Goods should be lightly sulphided during depilation in the fellmonger's yard as the presence of too high a proportion of sulphide leads to excessive swelling, attacks the hyaline layer and definitely injures the chance of the leather being absolutely suitable for rollers. The approximate strength of sodium sulphide in the depilatory paint should not be above 10° Twaddle for lambs and 16 for sheep.

Goods should be lightly limed as, when too plump the resultant leather is liable to lack the requisite lightness and appropriate degree of resiliency so necessary for this particular application. Concentration of sodium sulphide in the lime liquors preferably not exceeding 0.3 parts per 100 parts by volume of the solution and concentration of undissolved lime in suspension should not fall below five parts per 100.

Paddle liming is satisfactory provided the wheel does not rotate above 22 revolutions per minute. A good plan is to commence with a used, but not old, lime in pits and then to finish off with paddle work for the fresh lime liquor. Entire process can be completed in less than a week, i.e., allowing three days for used lime with two draws a day and three days for the new lime containing small proportion of sul-

phide. The used lime can also be strengthened up with a little sulphide but in all cases the maximum mentioned above must not be exceeded.

When properly limed, the pelts require trimming and fleshing. The latter operation must be done very thoroughly as the thorough removal of all extraneous flesh facilitates the penetration of tannin and the removal of natural fat during pressing in half tanned state if this is carried out. When fleshed, the pelts must be scudded, by hand preferably, or if by machine, then they need passing through twice. A thorough scudding not only removes all traces of hair or wool, but also succeeds in reducing the natural fat present in the goods and so eases the later degreasing process.

Both deliming and bating follow in the usual way on very much the same lines as with goods for full chrome clothing, taking care to scud after both deliming and pressing. Ammonium chloride, 0.5 per cent, is recommended for deliming, and temperature of both washing and deliming liquors must not exceed 75° F., otherwise there is a danger of goods being rendered rather tender. The paddle should be employed.

Pickling is recommended and the standard formula, namely, 10 per cent salt and one per cent sulphuric acid, gives excellent results. Paddle pickling is preferable to drum work and half an hour's processing is sufficient for all practical purposes.

After pickling goods can be degreased by means of one of the well known aqueous degreasing agents now on the market. Some of these give excellent results when used according to the manufacturer's directions and they are always preferable to the dangerous method of pressing half tanned goods, or degreasing goods in the crust state. The latter renders the leather liable to crack along the grain when subjected to any sudden strain in the dry biscuit condition.

After pickling or degreasing, goods need meshing up in the drum in a three per cent salt solution to which can be added the various tanning materials. Pure oak bark is still the finest tannin for roller leather but is now generally considered uneconomic to use it alone. A good blend of natural tannins can be built up from suitable extracts and bark infusions and the writer suggests a mixture of:

Oakwood extract
Chestnut extract
Valonia infusion
Oak bark infusion
Myrobalans extract.

In spite of all that has been said and written, it is possible to obtain excellent results from either drum or pit tannage provided proper precautions are taken to avoid broken or drawn grain. The most important of these precautions can be summarized as follows:

1. Reduce speed of drum or wheel to minimum consistent with proper circulation of goods and economical use of power.
2. See that strength of liquor, i.e., grammes of tannin per litre, is increased very gradually, preferably by means of an automatic feeding device.
3. Use some suitable agent to reduce surface tension. There are excellent chemical assistants on the market which do this and at the same time increase penetration.

To start off with, the stock solution should consist mainly of oak bark and valonia with only a little myrobalans extract. Then later on the oakwood and chestnut can be introduced and their concentrations increased. Last stages of tanning carried out mainly with oakwood and valonia.

Tanned goods need careful drying under natural conditions, then sorting in the crust warehouse. Shaving follows next and retanning. The latter consists of drumming goods

in a fairly strong sumach liquor which serves the actual purpose of cleaning the grain of the leather and completing the tanning process. Some tanners give the goods a preliminary retannage in strong liquor of the type previously used and then complete with a run in sumach. No matter which method is employed, it is essential that goods be laid away for two days before drying. This always improves the handle of the leather and is well worthwhile.

It may happen that a certain amount of clearing is necessary after shaving. This should be done with sulphuric acid in the usual way and "sumaching" can then follow. The addition of a small amount, five per cent, sumach in the acid solution is recommended as it helps in the clearing.

When goods are dry, they require stacking away in perfectly clean sawdust, then when properly conditioned they can be staked, trimmed, fluffed and brushed. Next follows whatever finishing is required, such as seasoning with milk and albumen finish, airing off, rolling, stoning and glazing. Marking with a frame, trimming, ironing, and final inspection for all stray hairs are subsequent operations for many tanners, but procedure differs widely according to particular requirements of the mill. The actual finishing of roller leather is quite simple and offers no difficulties whatever; what does offer difficulties is the preliminary preparation of a really sound leather and the production of a perfectly smooth grain.

XXIV

DRESSING HOGSKINS

HOGSKINS are rather troublesome to process owing to their characteristic dense structure and the difficulty of obtaining uniform penetration. To achieve this it is necessary to make full use of mechanical means, thus goods should, where possible, be processed in drums in preference to pits and paddles. The accentuation of the natural grain due to regular mechanical action generally improves the appearance of the leather, but at the same time care must be taken to avoid case hardening and spotty and uneven penetration. When testing for thoroughness of tanning process it is advisable to take several cuttings from different parts of the skin.

It is essential that the natural grease in hogskins should be removed as thoroughly as possible otherwise goods will never be able to be properly worked. The best method is to work the skins over the beam with a blunt fleshing knife before depilation. First soak the skins in water, 98° F., for 10 minutes, and then work out the saponified and emulsified grease. Next drum the skins in 1½ per cent solution of sodium carbonate for 10 minutes and repeat the processing until the maximum amount of grease is removed. Other alkalies may be used in preference to sodium carbonate if desired.

After the preliminary grease removal process has been completed the goods should be drummed in one per cent

solution of sodium sulphide at normal temperature until softened down; afterwards drumming in several changes of cold water should follow. Depilation can follow in the normal way. That is by painting with a lime and sulphide paste soaking in a strong solution of sulphide. The latter process is recommended and the goods can be drummed in a two per cent solution of sodium sulphide until the hair is thoroughly soft, pulpy and easy to remove. After passing through an unhairing machine or working over the beam with an unhairing knife the goods should be washed in clean water, taken out and allowed to drain, then fleshed by machine. This must be carried out very thoroughly so as to ensure the removal of all traces of fat and flesh and so facilitate penetration of lime.

Liming is best done with a saturated solution of lime in the paddle and the wheel should be kept revolving for a period of 25 minutes every five hours until the goods are thoroughly "plumped." They should then be refleshed and scudded. Before carrying out the latter process it is advisable to soak the skin in warm water, 95° F. for 10 minutes. Hand scudding on the grain and flesh sides is preferable to machine work.

Deliming is best carried out with ammonium chloride. It is a good plan to delime in the drum, using one per cent ammonium chloride and then to add the synthetic bate when the goods are just right, that is, when the cut surface is colorless to phenolphthalein but shows pink after leaving a few minutes. Any good proprietary bate may be used, satisfactory temperature being about 98° F. After bating, which may take as long as 24 hours, very thorough scudding should follow both on the flesh and grain sides so as to remove all hairs and also as much grease as possible; occasional dips in a tub of warm water always assists the removal of grease and stray hairs. Too much attention cannot be paid to these

preliminary processes as hogskin leather making is made or marred in the beam house. Some tanners process the leather in an aqueous grease removing solvent either prior to, or just after bating, and in capable hands this can give quite good results. The grease may, however, be removed by pressing half-way through the tanning process or petroleum degreasing after tanning when in the crust condition.

Any of the recognized processes of tanning may be successfully employed and in the case of vegetable tanning it is a good plan to start off with synthetic tanning agent and then to complete the leather making with natural tannin extracts, preferably rich in non-tans. J. A. Wilson, "Modern Practice In Leather Manufacture" gives a useful recipe employing a synthetic tanning agent:

"Put a pack of 1,000 lbs. pickled weight of stock into the tanning drum, start it running, and add a mixture of 50 lbs. of a commercial syntan and 100 lbs. salt in 120 gallons of water at 70° F. and run for 30 minutes. Dilute 300 lbs. of solid wattle extract with water to make 150 gallons at 170° F. Add 50 gallons of this liquor and run for one hour. Then add 50 gallons more and run for another hour. Then add the remaining 50 gallons and run for two hours longer. Allow the stock to remain in the drum over night, but have the drum run for one minute out of each hour during the night to guard against uneven coloring. Next morning haul out the stock, press it in a hydraulic press, wheel it to open up the skins and then split or shave it as may be required. Have on hand a stock of liquor of bisulphated quebracho extract containing four per cent of tannin. Put the stock back into the drum and cover with this liquor. Run until the skins are completely struck through in all parts, but for not less than two hours. Haul out the stock, pile it on trucks, and let it stand over night. Then wash in running water in a

drum at 80° F. for one hour, pile and send to be fat-liquored."

Promising results can be obtained by prior treatment with polymeric sodium metaphosphate, drumming bated goods in a 3.5 per cent solution, pH 2.9, for eight hours. Allow goods to drain for 24 hours, then wash them in the drum and tan with vegetable extracts in the usual way.

A mixture of chestnut, valonia, and myrobalans make a good sound blend for saddlery and wallet work. As mentioned previously, when the goods are half tanned they can be pressed in a hydraulic press, then each skin shaken out and thrown into the drum for further tanning. It is advisable to allow the goods to remain in a fairly strong sumach liquor for 48 hours, prior to draining, setting, oiling off and drying. Skins should be hung up to dry and not strained. When dry they are sorted (degreased if necessary), wet down for shaving or splitting, scoured on the table, washed, re-tanned, dyed and fat-liquored using a mixture of sulphonated neatsfoot and sulphonated cod liver oil, or a good egg yolk mixture or substitute.

Another method which works quite well is to alum tan the hogskins straight from the bate or drench, dry out and degrease in the petroleum degreasing plant. Afterwards, wet down in the drum and retan with a mixture of gambier, myrobalans extract and quebracho. Allow the sulphited tanned goods to lie in sumach liquor for three days before washing up, draining, setting, oiling off and drying in open sheds.

XXV

TANNER'S EPILOGUE

ALTHOUGH written primarily from the view point of the English tanner, the methods described by the author are capable of universal application and embrace many new ideas capable of considerable development; indeed, in some instances the writer is aware that his suggestions have already been adopted by manufacturers.

Before concluding the writer considers it desirable to summarize quite briefly the general principles governing the successful production of light leather; to touch upon the several lessons the industry has been forced to learn from the exigencies of war and to give publicity to these innovations and ideas which seem to have commercial possibilities.

Dealing first with raw material i.e., hides and skins, it is obvious that the greatest importance must be attached to the purchase of suitable skins; quality; size; weight; age and type. Of course in wartime the tanner has to be satisfied with what he can get and thinks himself lucky if he secures anywhere near his quota, but this advice is offered on the assumption that normal trading conditions will one day return.

A check-up by the writer in one well known light leather tannery showed that in an average pack of finished willow calf four to six per cent consisted of skins which fell well below the minimum standard of quality required and should,

therefore, never have been passed for this particular type of processing. Five to 10 per cent consisted of skins on the border line of rejection.

It has to be remembered that skins do not improve in quality during processing and, in many cases, faults are exaggerated. True, modern finishing processes can hide a multitude of smaller sins, but in an attempt to cover too many or too serious defects much time, labor and material may be wasted. There is no doubt in the writer's mind that, in the first instance, skins should be purchased with the utmost care and for clearly defined finishes, and secondly, sorting in the beamhouse and in the pickle should be sufficiently strict so as to ensure that the percentage of rejects in the finished warehouse falls below two per cent.

A few words should, at this juncture, be devoted to the storage of hides and skins. Dried and dry-salted goods must be kept under dry and cool conditions, otherwise degradation of the skin proteins will take place. Wet salted skins should be resalted every week and stored in small heaps in airy, cool sheds. Pelts from fellmongers and market skins must be put into work within 36 hours of arrival at the tannery.

In wartime, the greatest care and economy has to be exercised in the segregation, storage and ultimate disposal of all glue stock, such as trimmings, and all waste of possible value to the glue manufacturer. Glue is a munition of war and the need for this material has increased a thousand fold since the outbreak of hostilities.

The writer has many times emphasized the great importance of proper scientific control of the fundamental processes of leather manufacture, particularly soaking, liming, puering and pickling; the first two might well be said to be the key operations of the entire production of light leather. Use should be made of suitable disinfectants to keep down

the bacterial count of the soak liquor to a safe minimum; it might also be mentioned that the addition of fungicides to pickle liquors is recommended, particularly where pickled goods are to be retained in the salted condition for more than three months.

Owing to war conditions British tanners have been forced to use new natural tanning materials or, alternatively, to utilize new blends. This departure from standard and proved practice has been responsible for many headaches, but generally speaking a reasonably high standard of tanning has been achieved. Provided close scientific control of the tanning process is exercised there is no reason why the substitution of one type of tannin for another should make any difference to the quality of the leather produced. Some natural tannins are, what might be called "easy" tanning agents, that is, they are well balanced as regards tannins and non-tannins; others need compensation. The secret of success in evolving a suitable blend of extracts depends largely on the ability of the tanner to modify, by natural or artificial means, the astringency of high tannin content materials, such as quebracho, and to build up the low astringency materials to an economic level. The writer is of the opinion that after the war several new tanning materials will be widely adopted in preference to tannins of primary importance in pre-war days. It is also considered highly probable that greater use will be made in post-war years of preparatory agents possessing the property of regulating and accelerating the absorption of both natural and synthetic tannins. The phosphates are of particular interest in this respect, particularly for the pre-working of goods to be chrome tanned.

Pre-war experiments with organic chrome salts appear to offer some promise of commercial development when conditions return to normal. Such chemicals as chrome formate are capable of producing excellent leather and the writer has

prepared other compounds possessing very interesting properties, particularly the ability to feed impoverished skins. All these experiments must, however, be filed away for the time when sanity returns again to this old, troubled world.

The relationship of synthetic tanning materials to both natural and inorganic materials is most interesting. The former are not today regarded as rivals of vegetable tannins or chrome salts, but rather as most valuable "contributary" tanning agents. True, you can obtain commercially useful leather by the sole use of syntans, but a greatly superior leather is secured when these materials are used in conjunction with either chrome salts or natural tannins. A syntan-chrome tanning process produces the finest type of white leather, and synthetic agents used for the pre-tannage of sheep and goats to be subsequently tanned with extracts of quebracho and myrobalans help to produce a very satisfactory and cheap leather. There is good reason to believe that greater use will eventually be made of carefully blended mixtures of natural tannin extracts and synthetic materials, probably containing a smaller percentage of buffer salts to regulate the pH as well as various artificial filling agents, e.g., colloidal clays.

A word might be said at this juncture about the tannery plant. It takes no great prophetic power to foretell the growing use which will undoubtedly be made in post-war years of plastic materials in the construction of plant equipment. Paddles and vats of all kinds could be made of asbestos filled phenolic material and drums built of special phenol formaldehyde laminated sheet. Piping and hose of vinyl resins are other possibilities and may soon become well known to tanners because of their ability to give excellent service under the most difficult conditions. Mention might also be made of the use of phenolic and other coatings for iron containers to prevent staining of the leather in process-

ing and also to avoid any deterioration of the metal surface by deep pitting due to rust formation. It will well repay the tanner to give careful consideration to the benefits likely to be secured by close liaison with the plastics industry. New plastic materials and new industrial uses for standard resins may not at first appear of relevant interest but knowledge of developments in this important new industry may bring the solution to some vexing tanning problem or suggest an improvement in production. The writer insists that it will repay the tanner to watch the plastics industry.

Another industry that has, during the last 10 years, been of assistance to the tanner, is the soap industry. Production of new soapless detergents, such as the sulphonated fatty alcohols, has enabled better fatliquors to be produced and also made available a number of penetrants, levelling agents and wetting-down agents. It is no exaggeration to state that fatliquor can now be prepared possessing any required degree of penetration plus fibre lubrication. The old complaint that fatliquor emulsions broke down in acid solutions need not be heard any more as it is possible to prepare fatliquoring compounds of great stability and resistance to low pH.

In one of his earlier articles the writer described some experiments with specially oxidized cod liver oil for the production of chamois leather. Little appears to be done on these lines but excellent leather can be produced by merely drumming properly prepared fleshes in heavy emulsions of the oxidized oil, drying out the skins in a warm stove and then removing the excess of fatty material by drumming in an alkaline solution. The drying out of the process greatly accelerates the complete oxidation of the oil and insures completion of the tanning process. The method, will, it is hoped, be developed on a considerable scale as the better class leather produced is very suitable for clothing, slippers, and gloving and the lower grades for window cleaning and garage use.

Many new leather dyes have been developed by American and British manufacturers and the qualities of the dyes produced by the respective chemical industries compares favorably with any in the world. The 1914 World War saw Britain denuded of dyes and it was not until the end of the war that commercially sound dyes were being produced in bulk. Today, however, the British chemical industry is well developed and maintains close contact with its counterpart in America; such cooperation and collaboration makes for progress. Economy in the use of dyes and also in expensive finishes can be insured by employing suitable levelling agents. Many of these (mostly proprietary compounds) are now available and their use does not involve very much extra processing, merely drumming or paddle working for 10 to 15 minutes immediately prior to dying; in fact in most cases the same solution can be used. Some tanners regard these new materials as unnecessary luxuries but if they enable economies to be made in the use of dye and insure more level coloring, thus saving in finishing, then their employment is more than justified.

In the finishing of leather attention is being given to the plastic finishes, particularly acrylic polymers, which can now be obtained in the form of aqueous dispersions, and the vinyl resins. Incidentally some of the new rubber-like polymers obtained from petroleum hydrocarbons, e.g., polyisobutylene are receiving attention as leather finishes. For the proofing of leather against water, lethal gases, etc., use might well be made of the thioplasts (organic polysulphides) which, if suitably compounded, can be applied by spreading or brushing, or, if diluted (with cellosolve and ethylene glycol, etc.), sprayed.

It is worth mentioning here that the writer has given considerable attention to the use of chlorinated paraffin wax for the impregnation of upper leather required to afford the

maximum resistance towards the penetration of moisture. Various grades of materials produced by the chlorination of paraffin wax are now available and one particular type (approx. 27 per cent Cl content) is solid at normal temperatures but melts at about 25° C. Chlorinated paraffin wax is insoluble in water, alcohols, etc., and is stable and non-corrosive under ordinary conditions of storage. It may be heated to 100° C. in the presence of metals without decomposition. When exposed to sunlight for reasonable periods, chlorinated paraffin wax compounds are unaffected, but slight darkening occurs if the exposure is prolonged. Generally speaking these materials are inert and particularly resistant to acids and alkalies. Impregnation is simple and merely consists of immersing the dry leather in the melted wax, for a few minutes at a temperature of 35 to 40° C. and then setting-out the leather preparatory to quick cooling.

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